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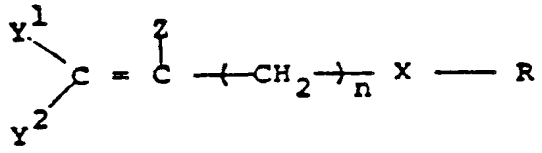

(I)

(57) Abstract

Polyhaloalkene compounds of formula (I), wherein X is sulfur, oxygen, nitrogen or methylene, Y^1 and Y^2 independently are fluorine, chlorine or bromine, Z is hydrogen or the same as Y^1 or Y^2, and n is 1-4; provided that: (A) when X is sulfur, R is thiazolyl substituted thienyl, optionally substituted thianaphthyl, optionally substituted thiazolinyl, optionally substituted thiadiazolyl, optionally substituted oxadiazolyl or 3,4,4- trifluoro-3-butenyloxycarbonyl-methyl; (B) when X is oxygen, R is $C(O)R^1$ wherein R^1 is perfluoroalkyl, optionally substituted phenyl, optionally substituted thienyl, optionally substituted furanyl, optionally substituted pyrrolyl or dihydrothiazolylthiomethyl; (C) when X is nitrogen, R taken with the nitrogen is an isothiocyanate, succinimide or saccharine group; and (D) when X is methylene, R is hydroxy. The compounds exhibit activity against plant nematodes and helminths that are indicators of animal anthelmintic activity and therefore are useful in agriculture and veterinary practice.

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PESTICIDAL POLYHALOALKENE DERIVATIVES

This invention relates to pesticidal polyhaloalkene derivatives and use for combatting infestations of nematodes in soil and in plant systems, particularly agricultural crops, and for combatting plant-destructive diseases caused wholly or in part by nematodes. The invention further concerns anthelmintic applications of the compounds.

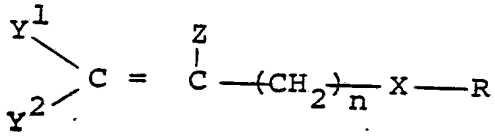
U.S. Patent 3,513,172 - Brokke and divisional patents thereof disclose nematicidal trifluorobutenyl derivatives of the formula

$$F_2C=CFCH_2CH_2-R$$

where R is selected from various substituents including some heterocyclics such as 2-thio-4-alkylthiazolyl. These and other patents reflect ongoing efforts of industry and governmental agencies to find and commercialize chemicals for combatting nematodes and nematode-induced plant diseases, to thereby reduce the substantial economic losses resulting from nematode infestations.

A new class of polyhaloalkene derivatives has now been found having high nematicidal activity and good soil mobility. In addition, the compounds exhibit control of a variety of nematodes, and in some cases systemic activity. The compounds also are effective against helminths that are indicators of animal anthelmintic activity.

The novel nematicidal compounds of the invention are polyhaloalkene derivatives of the formula (I):



wherein X is sulfur, oxygen, nitrogen or methylene, Y^1 and Y^2 independently are fluorine, chlorine or bromine, Z is hydrogen or the same as Y^1 or Y^2, and n is 1-4, preferably 1 or 2; provided that:

(A) when X is sulfur, R is thiazolyl, optionally substituted thienyl, optionally substituted thianaphthyl, optionally substituted thiazolinyl, optionally substituted thiadiazolyl, optionally substituted oxadiazolyl or 3,4,4-trifluoro-3-butenyloxycarbonylmethyl;

(B) when X is oxygen, R is $C(O)R^1$ wherein R^1 is perfluoroalkyl, optionally substituted phenyl, optionally substituted thienyl, optionally substituted furanyl, optionally substituted pyrrolyl or dihydrothiazolylthiomethyl;

(C) when X is nitrogen, R taken with the nitrogen is an isothiocyanate, succinimide or saccharine group; and

(D) when X is methylene, R is hydroxy.

Other aspects of the invention include methods of controlling nematode populations and arresting plant and animal diseases caused by nematodes and helminths, and nematicidal and anthelmintic formulations based on the polyhaloalkene derivatives. Typical nematode species controlled in accordance with the invention are the root-knot, stunt, lesion, cyst and C. elegans nematodes.

In subclasses A and B of the compounds of formula I above, available carbon atoms of the heterocyclic rings other than thiazolyl optionally may be substituted with any group or groups which are non-destruc-

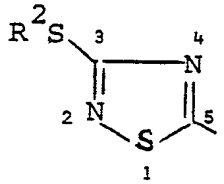
tive of the nematicidal or anthelmintic activity of the compounds. Typical substituents include aliphatic, aromatic and heterocyclic groups, halo, nitro, cyano, alkoxy, alkylthio, haloalkyl, haloalkoxy, halo-, nitro-, cyano- or alkoxy-substituted phenyl, polyhaloalkenylthio, phenylalkylthio, phenylthioalkylthio, propargylthio, cycloalkylmethylthio, and the like, further including straight and branched chain structures, and the various isomers of such substituents.

Throughout this specification the alkyl, alkenyl and alkynyl groups may contain 1-11 or more carbon atoms and may be straight chain or branched. Cycloalkyl groups may contain 3-8 or more carbon atoms. Preferably, alkyl, alkenyl, alkynyl and alkoxy are lower alkyl, lower alkenyl, lower alkynyl or lower alkoxy, meaning that these groups contain 1-8 carbon atoms, more preferably 1-4 carbon atoms such as methyl, propenyl and methoxy. Halo or halogen means fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine. Aromatic substituents include phenyl, naphthyl, anthracene, diphenyl, and the like.

Representative compounds of formula I are listed in Tables 1, 1a, 1b and 1c appended.

The preferred compounds of formula I are those of subclass A wherein R is defined as follows:

(1) R is a thiadiazolyl group of the structure:



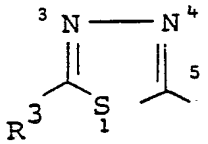
1,2,4-thiadiazol-5-yl or 1,2,4-thiadiazol-3-yl

wherein R^2 is 3,4,4-trifluoro-3-butenyl, or a phenylmethyl or phenylthiomethyl group each

optionally substituted with halogen or nitro. The R^2S- group may be in the 3- or 5-position of the 1,2,4-thiadiazole ring;

(2) R is a thiadiazolyl group as in (1) above but with iodo in place of R^2S;

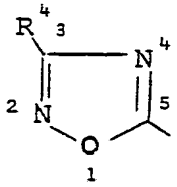
(3) R is a thiadiazolyl group of the structure:



1,3,4-thiadiazol-5-yl

wherein R^3 is aryl, arylalkyl, aryloxyalkyl, alkylthio, haloalkylthio, cyanoalkylthio, arylalkylthio, aryloxyalkylthio, arylthioalkylthio, heterocycloalkylthio, alkenylthio, haloalkenylthio, halocycloalkylalkenylthio, or an amino group mono- or disubstituted with members selected independently from alkyl, alkylcarbonyl, haloalkylcarbonyl, aryl, arylaminocarbonyl, arylalkylcarbonyl, arylalkoxycarbonyl and 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarbonyl;

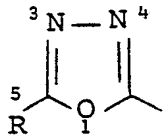
(4) R is an oxadiazolyl group of the structure:



1,2,4-oxadiazol-5-yl
or 1,2,4-oxadiazol-3-yl

wherein R^4 is aryl or arylalkyl substituted with chloro, fluoro, alkyl, haloalkyl, alkoxy, or nitro. The R^4 group may be in the 3- or 5-position of the 1,2,4-oxadiazole ring; or

(5) R is an oxadiazolyl group of the structure:



1,3,4-oxadiazol-5-yl

wherein R^5 is alkyl, haloalkyl, aryl, aryl-alkyl, aryloxyalkyl, arylthioalkyl, heterocyclo-alkyl, arylalkenyl or alkynyl (C_2-C_{11}).

Aryl and the heterocycles described in (3) and (4) above are optionally substituted with one or more groups selected independently from halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, cyano, nitro and phenyl. Aryl and the heterocycles described in (5) above are optionally substituted with one or more groups selected independently from halogen, alkyl, alkoxy, nitro, amino, hydroxy, acetyloxy and alkylaminocarbonyloxy.

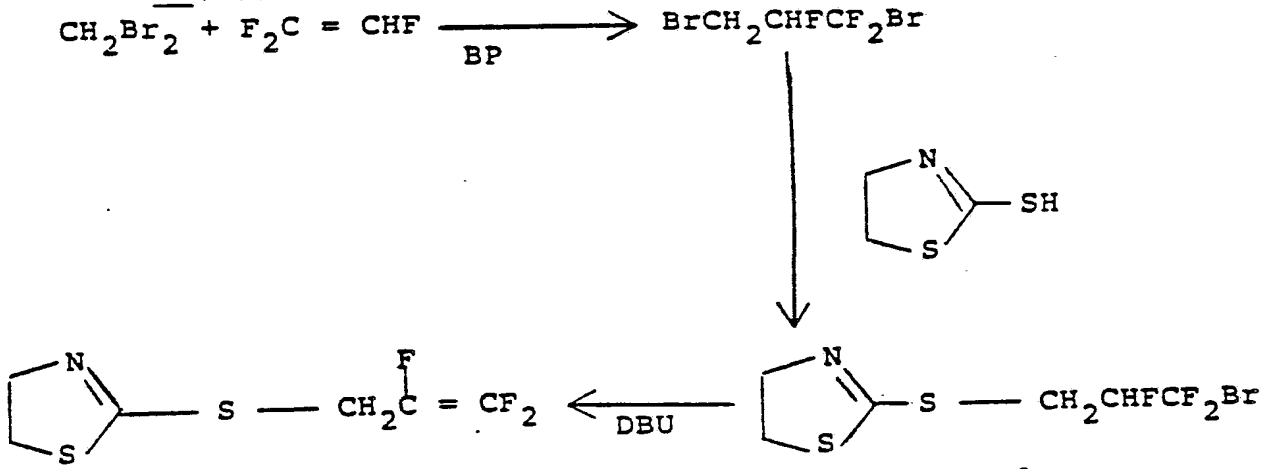
(6) R is a thiazolyl group.

Synthesis

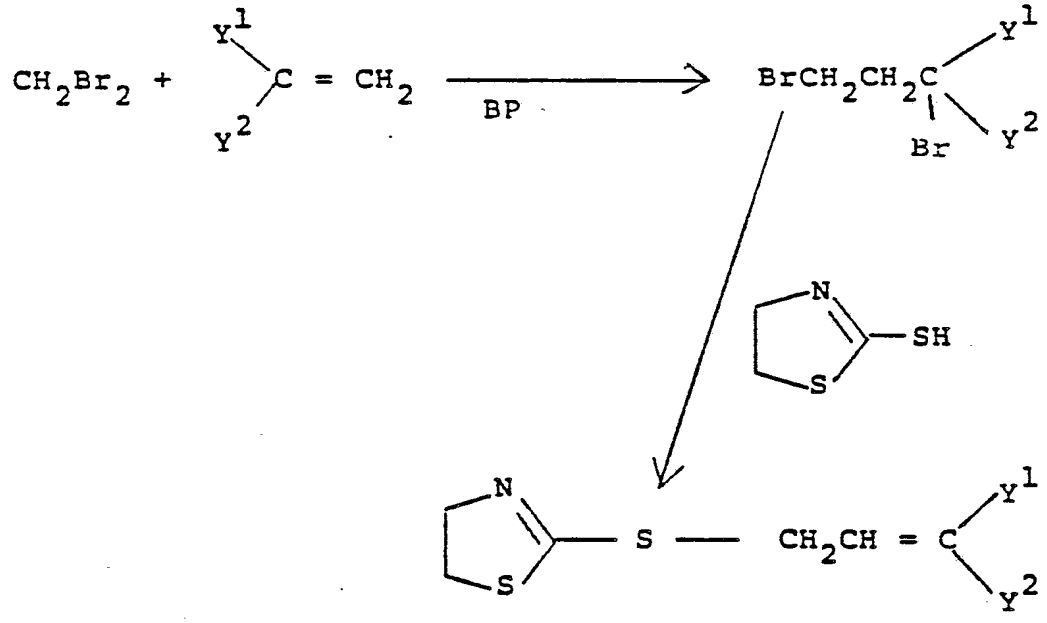
The compounds of formula I are prepared in a known manner. For example, a polyhaloalkene such as 4-bromo-1,1,2-trifluoro-1-butene is reacted with a mercaptothiazole (prepared by reaction of thiazole and elemental sulfur) or mercaptothiazoline in a reaction solvent medium containing sodium ethoxide to form the thiazolyl or thiothiazoline derivative of the poly-haloalkene. Examples 1, 2, 8-14, 16 and 17 below are representative of this and other reaction schemes for synthesis of the subclass A compounds of formula I (X = sulfur). Compounds of formula I wherein X is oxygen (subclass B) may be prepared as described in Examples 3 and 4. Similarly, the subclass C (X = nitrogen) and subclass D compounds (X = $-CH_2-$) are prepared as described in Examples 5 and 6 (subclass C) and 7 (subclass D).

Other polyhaloalkenes may be used in known ways to prepare other compounds of formula I. For example, trifluoroethylene can be chain-extended with methyl dibromide and the 1,3-dibromo-1,1,2-trifluoropropane product then reacted with a mercaptan to form a thio

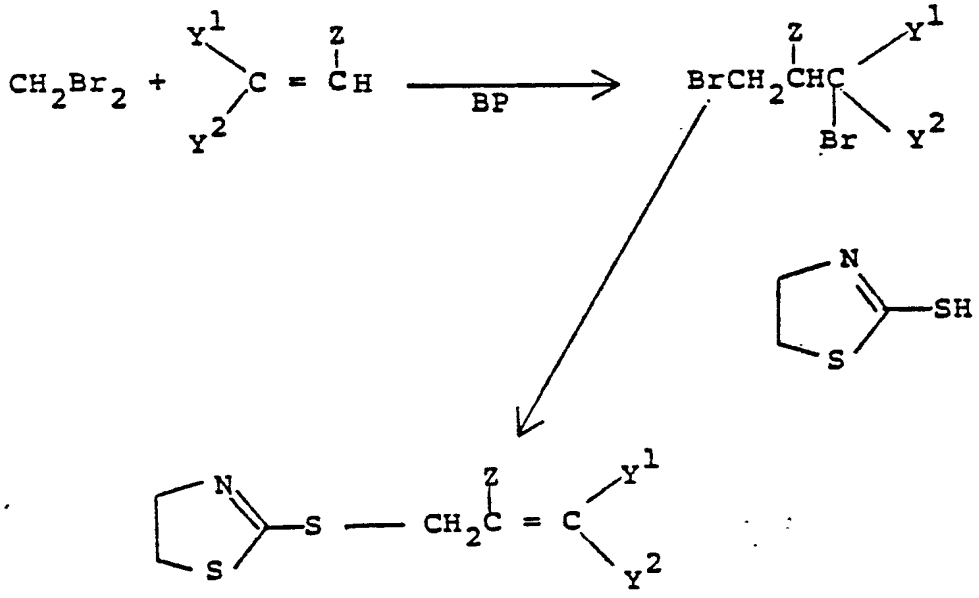
intermediate. The intermediate is then dehydrohalogenated, as follows, wherein "BP" is benzoyl peroxide and "DBU" is 1,8-diazabicyclo[5.4.0]undec-7-ene catalyst, as described by Tarrant and Tandon, J. Org. Chem. 34(4), 864 (1969):



Dihalopropene derivatives within the scope of formula I may be prepared by the following general reaction, wherein Y^1 and Y^2 are as defined above and one of Y^1 and Y^2 also may be hydrogen:



Trihalopropene derivatives also may be prepared in a manner and reaction similar to the Tarrant and Tandon scheme to form other compounds of formula I, wherein Y^1, Y^2 and Z are as defined in formula I:



Methods of preparing propenes, butenes and other alkenes having mixed halogen substituents and therefore useful in the invention for preparing compounds of formula I are described in a Ph.D. thesis of M. R. Lillyguist, University of Florida (1955), pages 9, 39, 59 and 60. It will be apparent, therefore, that the polyhaloalkenes and heterocyclic or other compounds used to prepare the compounds of formula I generally are known materials or can be synthesized by known procedures.

The following examples further describe methods of preparing the compounds of the invention. In the examples all parts and percentages are by weight and all temperatures are °C unless otherwise stated. The

products of Examples 1-9 correspond to compounds 1-9 listed in Tables 1 and 1b. Examples 10-17 identify the tabulated compounds to which they relate.

Example 1

2-(3,4,4-Trifluoro-3-butenylthio)-4,5-dihydrothiazole

Sodium ethoxide was prepared by stirring 0.25 gram (0.011 mole) of sodium metal in 30 ml of absolute ethanol. To this was added 1.2 grams (0.01 mole) of 2-mercaptothiazoline. The reaction mixture was stirred for one hour and the excess ethanol was removed under reduced pressure. The residue was dissolved in 35 ml of methyl ethyl ketone and 2.0 grams (0.01 mole) of 4-bromo-1,1,2-trifluoro-1-butene was added. The reaction mixture was stirred at ambient temperature for four hours, then concentrated under reduced pressure to a residue. The residue was dissolved in 50 ml of toluene and washed with three ml portions of water. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 1.7 grams of 2-(3,4,4-trifluoro-3-butenylthio)-4,5-dihydrothiazole as an oil. The nmr and the ir spectra were consistent with the proposed structure.

Example 2

5-Methylthio-2-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole

A solution of 2.0 grams (0.012 mole) of 2-mercapto-5-methylthio-1,3,4-thiadiazole in 25 ml of distilled acetone was added to a stirred mixture of 0.84 gram (0.006 mole) of potassium carbonate and 0.2 gram (0.001 mole) of potassium iodide in 25 ml of distilled acetone. With continued stirring 2.2 grams (0.012 mole) of 4-bromo-1,1,2-trifluoro-1-butene was added dropwise. Upon completion of addition the reaction mixture was heated under reflux for four hours.

The reaction mixture was cooled, filtered, and the filtrate concentrated under reduced pressure to a residue. The residue was dissolved in diethyl ether and washed with aqueous 5% sodium hydroxide. The organic layer was dried with magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 1.3 grams of 5-methylthio-2-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole as an oil. The nmr and the ir spectra were consistent with the proposed structure.

Example 3

(3,4,4-Trifluoro-3-butenyl) heptafluorobutyrate

(A) A stirred solution of 2.6 ml (0.02 mole) of heptafluorobutyric acid in 50 ml of water was warmed to 50°C and 5.1 grams (0.022 mole) of silver oxide was added. Upon completion of addition the reaction mixture temperature was maintained at 50-60°C for two hours. The reaction mixture was allowed to cool to ambient temperature, then it was filtered. The filtrate was concentrated under reduced pressure to give 6.4 grams of the silver salt of heptafluorobutyric acid as a solid.

(B) To a stirred mixture of 3.2 grams (0.01 mole) of the silver salt of heptafluorobutyric acid in 40 ml of diethyl ether was added dropwise 1.9 grams (0.01 mole) of 4-bromo-1,1,2-trifluoro-1-butene in 10 ml of diethyl ether. Upon completion of addition the reaction mixture was stirred for two hours at ambient temperature, then was heated under reflux for one hour. The ether solvent was removed by distillation and the residual oil distilled under reduced pressure to give 1.0 gram of (3,4,4-trifluoro-3-butenyl) heptafluorobutyrate; b.p. 25°C/4.0 mm Hg. The nmr spectrum was consistent with the proposed structure.

Example 4

(3,4,4-Trifluoro-3-butenyl) 4-chlorobenzoate

To a stirred solution of 1.6 grams (0.01 mole) of 4-chlorobenzoic acid in 35 ml of acetonitrile was added 1.5 ml (0.01 mole) of 1,8-diazabicyclo[5.4.0]-undec-7-ene, followed by 1.9 grams (0.01 mole) of 4-bromo-1,1,2-trifluoro-1-butene. The reaction mixture was heated under reflux for four hours then allowed to cool to ambient temperature. Water, 25 ml, was added to the reaction mixture, and the reaction mixture was extracted with three 20 ml portions of diethyl ether. The combined extracts were washed in succession with one 25 ml portion of water, two 25 ml portions of aqueous 5% sodium hydroxide and, finally, one 25 ml portion of water. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 1.2 grams of (3,4,4-trifluoro-3-butenyl) 4-chlorobenzoate as an oil. The nmr and the ir spectra were consistent with the proposed structure.

Example 5

N-(3,4,4-trifluoro-3-butenyl)succinimide

This compound was prepared in a manner analogous to that of Example 1 using 1.1 grams (0.01 mole) of succinimide, 1.9 grams (0.01 mole) of 4-bromo-1,1,2-trifluoro-1-butene, 0.25 gram (0.01 mole) of sodium metal, 30 ml of absolute ethanol and 20 ml of dimethylformamide. The yield of N-(3,4,4-trifluoro-3-butenyl)succinimide was 0.3 gram as an oil. The nmr and the ir spectra were consistent with the proposed structure.

Example 6

(3,4,4-Trifluoro-3-butenyl)isothiocyanate

(A) To a stirred solution of 10.0 grams (0.053 mole) of 4-bromo-1,1,2-trifluoro-1-butene in 50 ml of

dimethylformamide was added 10.4 grams (0.056) of the commercially available potassium salt of phthalimide. The reaction mixture was warmed to 50°C where it stirred for four hours. The reaction mixture was allowed to cool and 50 ml of chloroform was added. The mixture was poured into 200 ml of water. The aqueous layer was separated and extracted with two 50 ml portions of chloroform. The combined organic layers were washed with two 50 ml portions of aqueous 5% sodium hydroxide and one 50 ml portion of water. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 4.8 grams of N-(3,4,4-trifluoro-3-butenyl)phthalimide as an oil. The nmr spectrum was consistent with the proposed structure.

(B) A stirred solution of 4.2 grams (0.016 mole) of N-(3,4,4-trifluoro-3-butenyl)phthalimide and 1.0 ml (0.032 mole) of anhydrous hydrazine in 50 ml of methanol was heated under reflux for one hour. The reaction mixture was allowed to cool and the solvent removed under reduced pressure. The residue was taken up in 25 ml of water and 30 ml of concentrated hydrochloric acid. The reaction mixture was heated under reflux for two hours and then cooled to 0°C. A solid was removed from the reaction mixture by filtration. The filtrate was concentrated under reduced pressure to a residue. The residue was taken up in 50 ml of water and made basic with aqueous 10% sodium hydroxide. The mixture was extracted with two 25 ml portions of diethyl ether. The combined extracts were dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 0.4 gram of 4-amino-1,1,2-trifluoro-1-butene as an oil. The ir spectrum was consistent with the proposed structure.

(C) A stirred solution of 0.4 gram (0.004 mole) of 4-amino-1,1,2-trifluoro-1-butene in 25 ml of diethyl ether was saturated with gaseous hydrochloric acid. The reaction mixture was concentrated under reduced pressure to give 0.4 gram of 4-amino-1,1,2-trifluoro-1-butene hydrochloride as a solid. The nmr spectrum was consistent with the proposed structure.

(D) To a stirred solution of 0.4 gram (0.0027 mole) of 4-amino-1,1,2-trifluoro-1-butene hydrochloride in 15 ml of chloroform was added 0.3 gram (0.003 mole) of thiophosgene, followed by 0.7 ml (0.009 mole) of triethylamine. Upon completion of addition the reaction mixture was stirred at ambient temperature for three hours. The reaction mixture was then washed in succession with one 25 ml portion of water, two 25 ml portions of aqueous 5% sodium hydroxide, and, finally, one 25 ml portion of water. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 0.3 gram of (3,4,4-trifluoro-3-butenyl) isothiocyanate as an oil. The ir spectrum was consistent with the proposed structure.

Example 7

4,5,5-Trifluoro-4-penten-1-ol

(A) To a stirred mixture of 2.4 grams (0.1 mole) of magnesium turnings in 100 ml of diethyl ether was added 18.9 grams (0.1 mole) of 4-bromo-1,1,2-trifluoro-1-butene. Upon completion of addition the reaction mixture was heated under reflux until the reaction was complete. The reaction mixture was cooled to 0°C and 9.0 grams (0.2 mole) of carbon dioxide was bubbled in slowly. Upon completion of addition the reaction mixture was stirred for one hour, then 100 ml of aqueous 20% hydrochloric acid was added to destroy the excess magnesium. The reaction

mixture was extracted with three 40 ml portions of diethyl ether. The combined extracts were cooled and 40 ml of aqueous 25% sodium hydroxide was added slowly. The organic layer was separated and extracted with one 40 ml portion of aqueous 25% sodium hydroxide. The combined base layers were cautiously acidified with aqueous 20% hydrochloric acid. The mixture was extracted with two 100 ml portions of diethyl ether. The combined extracts were dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to give 6.9 grams of 4,5,5-trifluoro-4-pentenoic acid as an oil. The nmr and ir spectra were consistent with the proposed structure.

(B) To a stirred suspension of 0.4 gram (0.01 mole) of lithium aluminum hydride in 20 ml of diethyl ether was added dropwise a solution of 1.5 grams (0.01 mole) of 4,5,5-trifluoro-4-pentenoic acid in 30 ml of diethyl ether. Upon completion of addition the reaction mixture was stirred at ambient temperature for one hour, then 20 ml of water was added carefully. The mixture was filtered and the filtrate concentrated under reduced pressure to give 0.8 gram of 4,5,5-trifluoro-4-penten-1-ol as an oil. The nmr and the ir spectra were consistent with the proposed structure.

Example 8

3-Chloro-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole

(A) A stirred solution of 5.0 grams (0.026 mole) of dipotassium cyanoimidodithiocarbonate [prepared by the method of L.S. Wittenbrook et al, J. Org. Chem., 38, 3, 465 (1973)] in 19 ml of acetone and 22 ml of water was cooled to 0°C and 4.9 grams (0.026 mole) of 4-bromo-1,1,2-trifluoro-1-butene in 10 ml of acetone was added dropwise. Upon completion of addition the

reaction mixture was allowed to warm to ambient temperature where it stirred for 16 hours. The reaction mixture was concentrated under reduced pressure to a residual solid. The solid was dissolved in ethyl acetate and filtered. The filtrate was concentrated under reduced pressure, and the residual solid dried in a vacuum oven. The dried solid was dissolved in hot chloroform - ethyl acetate and filtered. The filtrate was concentrated under reduced pressure, and the residual solid dried in a vacuum oven to give 4.4 grams of potassium (3,4,4-trifluoro-3-butenyl) cyanoimidodithiocarbonate. The nmr spectrum was consistent with the proposed structure.

(B) A stirred solution of 2.0 grams (0.008 mole) of potassium (3,4,4-trifluoro-3-butenyl) cyanoimidodithiocarbonate in 10 ml of chloroform was cooled to 0°C and 1.2 grams (0.009 mole) of sulfuryl chloride was added dropwise. Upon completion of addition the reaction mixture was maintained at 0°C for one hour, warmed under reflux for 4 hours, then at ambient temperature for 16 hours. Stirring was continued throughout the 21 hour period. The reaction mixture was filtered and the filtrate concentrated under reduced pressure. The concentrate was passed through silica gel using diethyl ether as an eluent. The ether eluate was filtered and the filtrate concentrated under reduced pressure to a residual oil. The oil was dried in a vacuum oven to give 0.9 gram of 3-chloro-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole. The nmr and the ir spectra were consistent with the proposed structure.

Example 9

3-Bromo-5-(3,4,4-trifluoro-3-butenyl thio)-1,2,4-thiadiazole

A stirred solution of 3.0 grams (0.011 mole) of

potassium (3,4,4-trifluoro-3-butenyl) cyanoimidodithiocarbonate (prepared as in Example 8, Step A) in 25 ml of water was cooled to 0°C and 2.2 grams (0.014 mole) of bromine was added dropwise under a positive gaseous nitrogen pressure. Upon completion of addition the reaction mixture temperature was maintained at 0°C for one hour, then was allowed to warm to ambient temperature where it stirred for 16 hours. Sodium thiosulfate was added to the reaction mixture, which was then partitioned between chloroform and additional water. The chloroform layer was separated and dried with magnesium sulfate. The mixture was filtered and concentrated under reduced pressure to a residual oil. The oil was passed through silica gel using 4:1 - hexane:diethyl ether as an eluent. The eluate was concentrated under reduced pressure to give 1.1 grams of 3-bromo-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole as an oil. The nmr spectrum was consistent with the proposed structure.

Example 10 (Compound 25)

3,5-Di(3,4,4-Trifluoro-3-butenylthio)-1,2,4-thiadiazole

(A) A stirred solution of 16.0 grams (0.08 mole) of dipotassium cyanoimidodithiocarbonate (prepared as in Example 8, Step A) and 2.6 grams (0.08 mole) of sulfur in 425 ml of methanol was heated under reflux for 15 minutes. The reaction mixture was allowed to cool then was concentrated under reduced pressure to a residual solid. The solid was dried under reduced pressure to yield 18.1 grams of the dipotassium salt of 3,5-dimercapto-1,2,4-thiadiazole.

(B) A solution of 1.0 gram (0.004 mole) of the dipotassium salt of 3,5-dimercapto-1,2,4-thiadiazole in 35 ml of methyl ethyl ketone was stirred and 1.7 grams (0.009 mole) of 4-bromo-1,1,2-trifluoro-1-butene

was added. The reaction mixture was heated under reflux for two hours then allowed to cool to ambient temperature where it stirred for 18 hours. The reaction mixture was concentrated under reduced pressure to a residue. The residue was stirred in 25 ml of water and the mixture was extracted with two 25 ml portions of toluene. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield 1.1 grams of 3,5-di-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole as a liquid. The nmr spectrum was consistent with the proposed structure.

Example 11 (Compound 26)

3-(4-Nitrophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole

(A) A stirred solution of 24.7 grams (0.109 mole) of the dipotassium salt of 3,5-dimercapto-1,2,4-thiadiazole (prepared as in Example 10, Step A) in 200 ml of water was acidified with concentrated hydrochloric acid. The resultant solid was collected by filtration to yield 17.3 grams of wet 5-amino-1,2,4-dithiazol-3-thione; m.p. 217-220°C.

(B) A solution of 2.2 grams (0.055 mole) of sodium hydroxide in 7 ml of water and 20 ml of ethanol was stirred and 4.0 grams (0.027 mole) of 5-amino-1,2,4-dithiazol-3-thione was added portionwise. After all of the 5-amino intermediate was in solution, 4.7 grams (0.027 mole) of 4-nitrophenylmethyl chloride was added dropwise. Upon completion of addition the reaction mixture was stirred at ambient temperature for 16 hours. The reaction mixture was concentrated under reduced pressure to a residue. The residue was dissolved in 20 ml of water then extracted with two 25 ml portions of diethyl ether. The aqueous layer was acidified with concentrated hydrochloric acid to yield

a gummy solid. The solid was extracted from the aqueous layer with two 25 ml portions of ethyl acetate. The combined extracts were dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield a gummy solid. The solid was dissolved in methylene chloride and filtered to remove a small amount of insoluble material. The filtrate was concentrated under reduced pressure to yield 2.8 grams of 3-(4-nitrophenylmethylthio)-5-mercapto-1,2,4-thiadiazole as a solid. The nmr spectrum was consistent with the proposed structure.

(C) A solution of 0.25 gram (0.011 mole) of sodium in 35 ml of ethanol was stirred and 2.7 grams (0.0095 mole) of 3-(4-nitrophenylmethylthio)-5-mercapto-1,2,4-thiadiazole was added. Upon completion of addition the reaction mixture was stirred at ambient temperature for one hour. The ethanol solvent was removed under reduced pressure. The residue was dissolved in 35 ml of methyl ethyl ketone and 1.6 grams (0.0085 mole) of 4-bromo-1,1,2-trifluoro-1-butene was added. Upon completion of addition the reaction mixture was stirred for 16 hours, then was concentrated under reduced pressure to a residue. The residue was dissolved in 50 ml of toluene and washed with 25 ml of water, two 25 ml portions of aqueous 5% sodium hydroxide solution, and 25 ml of water. The organic layer was dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield a residual oil. The oil was dissolved in methylene chloride and passed through a column of silica gel. The eluate was concentrated under reduced pressure to yield 2.1 grams of 3-(4-nitrophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole. The nmr spectrum was consistent with the proposed structure.

Example 12 (Compound 30)

2-(1-Methylethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole

A solution of 22.5 grams (0.15 mole) of 2,5-dimercapto-1,3,4-thiadiazole in 200 ml of tetrahydrofuran was stirred and 21 ml (0.15 mole) of triethylamine was added dropwise. Upon completion of addition the reaction mixture was stirred at ambient temperature for 15 minutes, then 28.4 grams (0.15 mole) of 4-bromo-1,1,2-trifluoro-1-butene was added dropwise. Upon completion of addition the reaction mixture was heated under reflux for two hours. The cooled reaction mixture was concentrated under reduced pressure to a residue. The residue was stirred in 250 ml of diethyl ether and extracted with two 100 ml portions of aqueous 10% potassium hydroxide. The combined extracts were acidified with aqueous 10% hydrochloric acid, then were extracted with two 100 ml portions of diethyl ether. The combined ether extracts were dried with sodium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield, after drying, 35.6 grams of 2-mercapto-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole as a solid. The nmr spectrum was consistent with the proposed structure.

(B) In a manner analogous to Example 11, Step C, 1.3 grams (0.005 mole) of 2-mercapto-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole, 0.5 ml (0.005 mole) of 2-iodopropane, 0.15 gram (0.007 mole) of sodium were reacted in 35 ml of ethanol and 35 ml of methyl ethyl ketone by heating the mixture under reflux for five hours prior to stirring at ambient temperature for 16 hours. The yield of 2-(1-methylethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole was 1.3 grams as a liquid. The nmr spectrum was consistent with the proposed structure.

Example 13 (Compound 37)

2-(4-Chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole

(A) A stirred solution of 8.1 grams (0.048 mole) of 4-chlorobenzoic acid hydrazide in 300 ml of triethyl orthoformate was heated under reflux for 16 hours. The excess triethyl orthoformate was removed by distillation and the residual solid was stirred with petroleum ether to yield 7.7 grams of 2-(4-chlorophenyl)-1,3,4-oxadiazole; m.p. 129°C. The nmr spectrum was consistent with the proposed structure.

(B) Under a nitrogen atmosphere, a solution of 17 grams (0.084 mole) of phosphorus pentasulfide in 100 ml of dry xylene was stirred and 7.6 grams (0.042 mole) of 2-(4-chlorophenyl)-1,3,4-oxadiazole was added. Upon completion of addition the reaction mixture was heated under reflux for 30 hours. The reaction mixture was cooled and 100 ml of water was added dropwise. The mixture was filtered through diatomaceous earth to separate the organic and aqueous phases. The organic phase (the filtrate) was extracted with an aqueous 10% potassium hydroxide solution. The extract was acidified with an aqueous 5% hydrochloric acid solution, and then was extracted with diethyl ether. The ether extract was concentrated under reduced pressure to yield 0.3 gram of 2-(4-chlorophenyl)-5-mercapto-1,3,4-thiadiazole; m.p. 178°C.

(C) In a manner analogous to Example 2, 0.3 gram (0.0015 mole) of 2-(4-chlorophenyl)-5-mercapto-1,3,4-thiadiazole, 0.4 gram (0.002 mole) of 4-bromo-1,1,2-trifluoro-1-butene, 0.2 gram (0.0015 mole) of potassium carbonate, and 0.05 gram of potassium iodide were reacted in 9 ml of methyl ethyl ketone. The yield of 2-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-

1,3,4-thiadiazole was 0.1 gram; m.p. 68-69°C. The nmr spectrum was consistent with the proposed structure.

Example 14 (Compound 39)

3-(4-Chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole

(A) A stirred solution of 4.1 grams (0.03 mole) of 4-chlorobenzonitrile, 2.1 grams (0.03 mole) of hydroxylamine hydrochloride, and 2.1 grams (0.015 mole) of potassium carbonate in 10 ml of water and 100 ml of ethanol was heated under reflux for 16 hours. The reaction mixture was cooled and 50 ml of water was added. The ethanol solvent was removed under reduced pressure. The concentrate was cooled in an ice bath and the resultant solid collected by filtration. The solid was dried to yield 4.4 grams of N-hydroxy-imido-4-chlorobenzamide; m.p. 122-130°C.

(B) A solution of 4.4 grams (0.028 mole) of N-hydroxyimido-4-chlorobenzamide in 50 ml of diethyl ether was stirred and 0.55 ml (0.007 mole) of thio-phosgene was added dropwise. Upon completion of addition the reaction mixture was stirred at ambient temperature for 15 minutes then was heated under reflux for one hour. The reaction mixture was cooled and filtered to collect bis 0,0'-thiocarbonyl(4-chloro-N-hydroxybenzenecarboximidamide). A 100% yield was assumed.

(C) A solution of 10.0 grams (0.25 mole) of sodium hydroxide in 90 ml of water was stirred and 5.4 grams (0.14 mole) of bis 0,0'-thiocarbonyl(4-chloro-N-hydroxybenzenecarboximidamide) was added. Upon completion of addition the reaction mixture was heated under reflux for one hour. The reaction mixture was cooled and extracted with two 50 ml portions of diethyl ether. The aqueous layer was acidified with concentrated hydrochloric acid. The resultant preci-

pitate was collected by filtration, washed with water, and dried to yield 1.0 gram of 3-(4-chlorophenyl)-5-mercapto-1,2,4-oxadiazole; m.p. 139-156°C, dec. The nmr spectrum was consistent with the proposed structure.

(D) In a manner analogous to Example 2, 0.7 gram (0.003 mole) of 3-(4-chlorophenyl)-5-mercapto-1,2,4-oxadiazole, 0.6 gram (0.003 mole) of 4-bromo-1,1,2-trifluoro-1-butene, 0.2 gram (0.0015 mole) of potassium carbonate, and 0.1 gram of potassium iodide were reacted in 40 ml of distilled acetone. The yield of 3-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole was 0.3 gram; m.p. 49-52°C. The nmr spectrum was consistent with the proposed structure.

Example 15 (Compound 43)

5-(3-4,4-Trifluoro-3-butenylthio)-1,3,4-oxadiazole

(A) A solution of 25 grams (0.147 mole) of 4-chlorophenylacetic acid in 250 ml of acetonitrile was stirred and 15.0 grams (0.0147 mole) of bromoethane, followed by 22.0 grams (0.147 mole) of 1,8-diazabicyclo[5.4.0]undec-7-ene, were added. Upon completion of addition the reaction mixture was cooled in a water bath while being stirred for 18 hours. The reaction mixture was concentrated under reduced pressure to one-half volume and then was added to 50 ml of water. The mixture was extracted with two portions of diethyl ether. The combined extracts were dried with magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield 18.2 grams of ethyl (4-chlorophenyl)acetate.

(B) A stirred solution of 18.2 grams (0.091 mole) of ethyl (4-chlorophenyl)acetate and 10 ml of hydrazine hydrate in 10 ml of ethanol was heated under reflux for one hour during which time a solid preci-

pitated. The solid was collected by filtration to yield, when dried, 14.9 grams of 4-chlorophenylacetic acid hydrazide; m.p. 159-161°C. The nmr spectrum was consistent with the proposed structure.

(C) A stirred solution of 7.0 grams (0.038 mole) of 4-chlorophenylacetic acid hydrazide, 3.0 grams (0.039 mole) of carbon disulfide and 2.8 grams (0.050 mole) of potassium hydroxide in 10 ml of water and 200 ml of ethanol was heated under reflux for four hours. The ethanol was removed under reduced pressure. The concentrate was taken up in water and the mixture washed with diethyl ether. The aqueous layer was acidified with aqueous 5% hydrochloric acid and then was extracted with diethyl ether. The extract was dried with magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to yield 3.9 grams of 2-(4-chlorophenylmethyl)-5-mercapto-1,3,4-oxadiazole; m.p. 115°C. The nmr spectrum was consistent with the proposed structure.

(D) In a manner analogous to Example 2, 2.4 grams (0.011 mole) of 2-(4-chlorophenylmethyl)-5-mercapto-1,3,4-oxadiazole, 2.0 grams (0.011 mole) of 4-bromo-1,1,2-trifluoro-1-butene, 1.5 grams (0.011 mole) of potassium carbonate and 0.5 gram of potassium iodide were reacted in 45 ml of acetone. The yield of 2-(4-chlorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole was 1.5 grams as a liquid. The nmr spectrum was consistent with the proposed structure.

Example 16 (Compound 230)

Synthesis of 2-(3,4,4-trifluoro-3-butenylthio)thiazole

Under a nitrogen atmosphere, a stirred solution of 2.0 grams (0.024 mole) of thiazole in 30 ml of dry tetrahydrofuran is cooled to -65°C and 16 ml of 1.55

molar n-butyllithium is added dropwise. Upon completion of addition the reaction mixture is stirred for 45 minutes and 0.8 gram (0.024 mole) of elemental sulfur is added portionwise. The reaction mixture is stirred for an additional one hour, the temperature then being adjusted to -60°C, and 4.5 grams (0.024 mole) of 4-bromo-1,1,2-trifluoro-1-butene is added dropwise. Upon completion of addition the reaction mixture is stirred for three hours during which time it is allowed to warm to ambient temperature. The solvent is removed under reduced pressure. The residue is dissolved in diethyl ether and washed with two portions of an aqueous solution saturated with sodium chloride. The organic layer is dried with magnesium sulfate and filtered. The filtrate is concentrated under reduced pressure to a residual semi-solid. The semi-solid is subjected to column chromatography on silica gel. Elution is accomplished with 1:1 - hexane:diethyl ether. The appropriate fractions are combined and concentrated under reduced pressure to give 0.4 gram of 2-(3,4,4-trifluoro-3-butenylthio) thiazole as an oil. The nmr and ir spectra are consistent with the proposed structure.

Example 17 (Compound 231)

Synthesis of 2-(2,3,3-trifluoro-2-propenylthio)thiazole

(A) A stainless steel autoclave is charged with 50 grams (0.6 mole) of trifluoroethylene, 300 grams (1.7 moles) of dibromomethane, and 5 grams (0.02 mole) of benzoyl peroxide. The reaction mixture is stirred and heated at 100°C for six hours, then is cooled to -70°C. The autoclave is opened and the reaction mixture fractionally distilled. The appropriate fractions are combined to give 1,3-dibromo-1,1,2-trifluoropropane.

(B) Under a nitrogen atmosphere a stirred solution of 20 grams (0.24 mole) of thiazole in 300 ml of dry tetrahydrofuran is cooled to -65°C and 160 ml of n-butyllithium (1.55 molar) is added dropwise. Upon completion of addition the reaction mixture is stirred for 45 minutes and 8.0 grams (0.24 mole) of elemental sulfur is added portionwise. Upon completion of addition the reaction mixture is stirred for one hour and, at -60°C. 61.4 grams (0.24 mole) of 1,3-dibromo-1,1,2-trifluoropropane is added dropwise. Upon completion of addition the reaction mixture is allowed to warm to ambient temperature where it stirs for three hours. The reaction mixture is concentrated under reduced pressure to a residue. The residue is dissolved in diethyl ether and is washed with two portions of aqueous sodium chloride. The organic layer is dried with magnesium sulfate and filtered. The filtrate is concentrated under reduced pressure to a residue. The residue is purified by column chromatography to give 2-(3-bromo-2,3,3-trifluoropropylthio)-thiazole.

(C) A stirred solution of 2.9 grams (0.01 mole) of 2-(3-bromo-2,3,3-trifluoropropylthio)thiazole and 1.5 grams (0.01 mole) of 1,8-diazabicyclo[5.4.0]-undec-7-ene in 40 ml of toluene is heated under reflux for two hours. The solvent is removed by distillation and the residue is purified by column chromatography to give 1.1 grams of 2-(2,3,3-trifluoro-2-propenylthio)thiazole.

The appended Tables 1, 1a, 1b and 1c list compounds prepared as in the foregoing Examples. In Tables 1a and 1c the compounds are those of formula I wherein Y^1, Y^2 and Z are fluoro, based upon the use of 4-bromo-1,1,2-trifluoro-1-butene as the starting material in the synthesis.

Pesticidal Use

The compounds of the invention can be used against a variety of pests that attack plants and animals. In agriculture, they are useful as nematicides, particularly against plant-parasitic nematodes and "free-living" nematodes, i.e., nematodes not dependent on any specific plant or other host. An example of the latter is the microbivorous nematode Caenorhabditis elegans. This nematode will feed on bacteria such as Escherichia coli and is used as a screen for both agricultural and veterinary nematicides or anthelmintics.

When used as anthelmintics, in veterinary treatments for treatment of infestations of Ascaris lumbricoides (roundworm in pigs) for example, the compounds may be administered orally, parenterally or topically either alone but more usually in a pharmaceutically acceptable carrier, to provide an appropriate dosage. Such carriers include one or more of water, gelatine, sugars, starches, organic acids such as stearic or citric acid and salts thereof, talc, vegetable fats or oils, gums, glycols and other excipients, for administration as solids (e.g., tablets or capsules) or liquids (e.g., solutions, suspensions or emulsions). The compositions may also contain preservatives, stabilizers, wetting or emulsifying agents, buffers, salts and other therapeutic agents. The compositions may be formulated by conventional methods to contain about 5 to 95% by weight of the anthelmintic compound, preferably about 25 to 75% by weight. Further guidance to anthelmintic activity, formulations and modes of treatment, utilizing the compounds of the invention, is available from publications on the subject, such as the article "Chemotherapeutics, Anthelmintic" in Kirk-Othmer, Encyclopedia of Chemical

Technology, Third ed., 5 451-468, and articles cited therein, and in the patent literature, such as U.S. Patent 3,576,892, col. 3, lines 29-56.

In using the compounds of the invention as agricultural nematicides, the compounds, like most agricultural chemicals, are generally not applied full strength, but are formulated with agriculturally acceptable carriers and various additives normally employed for facilitating the dispersion of active ingredients, optionally with other active ingredients, recognizing that the formulation and mode of application of a toxicant may affect the activity of the material. The present compounds may be applied, for example, as powders or liquids, the choice of application varying with the nematode species and environmental factors present at the particular locus of infestation. Thus, the compounds may be formulated as granules, dusts, wettable powders, emulsifiable concentrates, solutions, suspensions, dispersions, controlled release compositions, and the like.

A typical formulation may vary widely in concentration of the active ingredient depending on the particular agent used, additives, carriers or other active ingredients used, the nematode species to be controlled, and the desired mode of application. With due consideration to these factors, the active ingredient of a typical formulation may, for example, suitably be present at a concentration of from about 0.5% up to about 99.5% by weight of the formulation. Surface active agents, if employed in the formulation, may be present at various concentrations, suitably in the range of 1 to 30% by weight.

Dusts are admixtures of the active ingredient with finely divided solid carriers and/or diluents such as talc, natural clays, kieselguhr, pyrophyllite,

chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulfur, lime, flours, and other organic and inorganic solid carriers. These finely divided formulations generally have an average particle size of less than about 50 microns (325 mesh, Standard U.S. Sieve Series). In most cases, the active ingredient will be present in dust formulations at a concentration in the range of 1 to 15%, and occasionally from 1% to about 30%, the balance of the composition typically comprising one or more agriculturally acceptable inerts as adjuvant, carrier, or diluent.

The nematicidal compounds of the invention may also be formulated as wettable powders. These formulations are in the form of finely divided particles which disperse readily in water or other liquid vehicles. The wettable powder is ultimately applied as a dry dust or a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas, and other highly absorbent or adsorbent inorganic diluents. The concentration of active ingredient in wettable powders is dependent upon physical properties of the active ingredient and the absorbency of the carriers. Liquids and low melting solids (mp less than 100°C) are suitably formulated in the concentration range of 5 to 50% by weight; usually 10 to 30%; high melting solids (mp greater than 100°C) being formulated in the range of 5 to 95% by weight, usually 50 to 85%. An agriculturally acceptable carrier or diluent, frequently including a small amount of a surfactant to facilitate wetting, dispersion and suspension, accounts for the balance of the formulation.

Microencapsulated or other controlled release

formulations may also be used for application of compounds in accordance with this invention.

Emulsifiable concentrates (EC's) are homogeneous liquid compositions, usually containing the active ingredient dissolved in a liquid carrier. Commonly used liquid carriers include xylene, heavy aromatic naphthas, isophorone, and other nonvolatile or slightly volatile organic solvents. For application of the nematicide, these concentrates are dispersed in water, or other liquid vehicle, forming an emulsion, and are normally applied as a spray to the area to be treated. The concentration of the essential active ingredient in EC's may vary according to the manner in which the composition is to be applied, but, in general, is in the range of 0.5 to 95%, frequently 10 to 80%, by weight of active ingredient, with the remaining 99.5% to 5% being surfactant and liquid carrier.

Flowables are similar to EC's except that the ingredient is suspended in a liquid carrier, generally water. Flowables, like EC's, may include a small amount of a surfactant, and contain active ingredient in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing or emulsifying agents used in these formulations include, but are not limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium or calcium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition

products of such esters; addition products of long-chain mercaptans and ethylene oxide; and addition products of alkylphenols such as nonylphenol and ethylene oxide. Many other types of useful surface-active agents are available in commerce. The surface-active agent, when used, normally comprises from 1 to 15% by weight of the nematicidal composition.

Other useful formulations include simple solutions of the active ingredient in a relatively non-volatile solvent such as corn oil, kerosene, propylene glycol, or other organic solvents. This type of formulation is particularly useful for ultra-low volume application.

The concentration of active ingredient in use dilution is normally in the range of about 2% to about 0.1%. Many variations of spraying, dusting, and controlled or slow release compositions in the art may be used by substituting or adding a compound of this invention to compositions known or apparent to the art.

The compositions may be formulated and applied with other suitable active ingredients, including other nematicides, insecticides, acaricides, fungicides, plant regulators, herbicides, fertilizers, etc.

In applying the foregoing chemicals, an effective nematode controlling amount of active ingredient must be applied, sometimes referred to herein as a "nematicidal amount." While the application rate will vary widely depending on the choice of compound, the formulation and mode of application, the plant species being protected and the planting density, a suitable use rate may be in the range of 0.5 to 25 kg/hectare, preferably 1 to about 20 kg/hectare.

The compounds of this invention are usually applied by incorporating a formulation thereof into the soil in which plants or agricultural crops are or

are to be planted, i.e., the locus of infestation. This may be achieved by incorporating the compounds into the soil or by broadcasting the formulation over the planted area or the area to be planted or by limiting the application to a small area or band in the root zone where plants are or are to be planted. It will be readily apparent where the latter method is employed that a nematicidal amount, that is, a nematicidal concentration in the soil, must be applied to the root zone. A suitable concentration for this purpose is in the range of 0.1 to about 50 parts by weight of compound of the invention per million parts of soil.

However, in a significant aspect of the invention, it has been found that certain of the polyhaloalkene derivatives of the invention have efficacy against nematodes by foliar application, i.e., the compounds are systemic nematicides. This aspect is exemplified hereinafter.

The following are specific examples of formulations which may be utilized in accordance with the present invention. In these formulations the percentages are wt/wt.

1. Typical dust formulation:

Test Compound	5%
Base	95%
96% Attaclay	
2% highly purified sodium lignosulfonate (100%)	
2% powdered sodium alkylnapthalene sulfonate (75%)	

2. Typical emulsifiable concentrates:

(A) Test Compound	5.0%
Emulsifier A	4.0%
Emulsifier B	0.4%
Emulsifier C	0.8%
Emulsifier D	1.3%
Refined xylene solvent	88.5%

Emulsifier A is the anionic calcium salt of dodecylbenzene sulfonate. Emulsifier B is a nonionic 6-molar ethylene oxide condensation product of nonylphenol. Emulsifier C is a nonionic 30-molar ethylene oxide condensation product of nonylphenol. Emulsifier D is a nonionic paste of 100% polyalkylene glycol ether.

(B) Test compound	21.3%
Emulsifier A	4.2%
Emulsifier B	0.5%
Emulsifier C	0.9%
Emulsifier D	1.4%
Refined xylene solvent	71.7%
(C) Test compound	5.0%
Emulsifier E	4.0%
Emulsifier F	3.0%
Emulsifier G	3.0%
Dormant spray oil solvent (non-volatile)	85.0%

Emulsifier E is an oil-soluble nonionic blend of polyoxyethylene ethers commercially available under the trademark and designation "T Mulz 808A". Emulsifier F is a formulated nonionic concentrate commercially available under the trademark and designation "FloMo 200-4". Emulsifier G is the anionic free acid of a complex organic phosphate ester commercially available under the trademark and designation "Gafac RE-410".

3. Typical granule formulations:

(A) Test compound (technical)	5.0%
Attapulgite carrier/diluent	95.0%

The carrier/diluent is a 20/40 or 60/90 mesh hydrated aluminum magnesium silicate of low volatile matter having 2% free moisture.

(B) Test compound (technical)	5.0%
Ground corn cobs, 14/40 mesh	95.0%
(C) Test compound (as emulsifiable concentrate 2(B) above)	23.5%
Attapulgite carrier/diluent [3(A) above]	76.5%

4. Typical solution formulation:

Test compound	0.3%
Acetone	55.9%
Water	43.8%

Biological Testing

Compounds of this invention were tested as follows for nematicidal and anthelmintic activity as dust formulations (initial and residual activity) and as acetone/water formulations (systemic activity). The formulations are described above.

1. Initial Root-Knot Nematicidal Activity

The activity against root-knot nematode (Meloidogyne incognita) was determined by incorporating the compound of the invention in nematode infested soil at rates in the range of 10 ppm to 0.078 ppm of compound. Several tomato or cucumber seedlings were planted in the nematode infested soil. Two weeks after planting the test pots were evaluated to ascertain the degree of galling (swelling) on the roots of the plants, indicating the control provided by the test chemical.

The results expressed as percent control (determined by knot index) are set forth as averages in

Table 2 (appended). Knot index is a numerical designation assigned at evaluation, having the following meanings:

Knot Index	Observations
0	No swellings - complete control
1	75% less swellings than control plants
2	50% less swellings than control plants
3	25% less swellings than control plants
4	About same as control plants - no control.

Percent control is related to knot index as follows:

Knot Index	Percent Control
0	100
1	75
2	50
3	25
4	0

When the Knot Index is between 0 and 1 it is further subdivided as follows to indicate how close the percent control is to 75% or 100%:

Knot Index	Percent Control
0.8	80
0.5	90
0.1-0.4	95-99

The results demonstrate that compounds of this invention are highly effective against root-knot nematodes at the application rates tested.

2. Residual Root-Knot Nematicidal Activity

The ability of nematicidal compounds of the invention to control root-knot nematode infestations in soil over a period of time after treatment was evaluated. Dust formulations of test compound (5%) were incorporated into soil samples at test compound rates of 5 and 10 ppm. Subsequently, the treated soil

samples were inoculated with nematode inoculum at weekly intervals, and Knot Index and Percent Control determined on seedlings planted in the soil samples. Specifically, soil treated with test compound was placed in 7.6 cm diameter fiber pots and stored in a greenhouse. At one, two and four weeks post-treatment, the appropriate number of pots was infested with root-knot nematode eggs and larvae. A cucumber or tomato seedling was planted in each pot and evaluated approximately two weeks after the soil infestation to obtain the test results reported in Tables 3 and 3a appended. The data shows that as compared with untreated, but nematode-inoculated control soil, planted with seedlings (which showed no nematode control), substantial residual activity was exhibited with most of the test compounds at the application rates tested.

3. Stunt Nematode Test

The procedure was substantially the same as in the initial root-knot nematode tests described above except that rates of application of formulated compound were 2.5 and 5 ppm in soil containing a corn seedling, with subsequent inoculation of the soil with combined larvae and adult stunt nematodes. The samples were evaluated approximately four weeks after infestation. The results (Tables 4 and 4a appended) indicate good control at the test application rates as compared with untreated samples where no control was observed. "Percent control" means the difference between average population counts between untreated and treated samples, divided by average population count of untreated sample, multiplied by 100.

4. Lesion Nematode Test

The procedure was substantially the same as in the stunt nematode test described above except that

pea seedlings were used. The results (Table 5 appended) show good control with many of the compounds at the application rates tested as compared with untreated samples (no control). "Percent Control" is defined as follows:

$$\frac{\left(\frac{\text{Population Count in Check}}{\text{Wt of Roots in Check Plant}} - \frac{\text{Population Count in Trtmt}}{\text{Wt of Roots in Treated Plants}}\right)}{\frac{\text{Population Count in Check}}{\text{Wt of Roots in Check Plant}}} \times 100$$

5. Cyst Nematode Test

The procedure was substantially the same as described in the stunt nematode test except soybean seedlings were used. "Percent Control" (Table 6 appended) is as defined in the stunt nematode test results. The data indicate good control by most of the compounds at the application rates tested.

6. Soil Mobility

The ability of nematicidal compounds of the invention to move through nematode-infested soil and to control the nematodes was evaluated by incorporating 5% dust formulations of test compound at 30 ppm rates into pots of root-knot nematode infested soil, and subsequently eluting the soil with 15 cm of water (equivalent to 15 cm of rainfall) into a series of two or more pots of untreated, but nematode-infested, soil. Specifically, the pots were 8 cm diameter plastic pots containing a 10 cm^3 layer of sand over a coarse grade filter paper disc. Sufficient soil was placed over the sand to fill the pots, and a second filter paper disc was placed over the soil. Each test compound-treated pot was nested over a series of two or more pots containing untreated, but nematode-

infested soil, also containing sand filter paper discs as described for the treated soil pots. Fifteen cm of water was slowly dripped into the top pots and the pots were allowed to drain for 16-18 hours to remove excess water. The top filter of each pot was then removed and the pots were planted with a cucumber or tomato seedling. The seedlings were evaluated approximately two weeks after planting to give the test results reported in Tables 7 and 7a appended. The data indicate good soil mobility and nematicide control at the application rates tested as compared to untreated systems which showed no nematode control. "Knot Index" and "Percent Control" are as defined in the initial root-knot nematode tests above.

8. Systemic Activity

Compounds of the invention were tested for basipetal systemic activity against the root-knot nematode. In this test, tomato plants are grown in 10.2 cm diameter fiber pots containing steam-pasteurized soil mix (50% soil, 50% sand) until 4-6 true leaves appear. Three of the pots are then placed on a turntable in a spray hood and the plants sprayed with 50 ml of water/acetone solution containing the test compound. The soil surface is covered during the spraying to prevent spraying of the soil. After treatment, the potted plants are placed in a lighted drying chamber. The plants are then grown in a growth chamber at 25°C for three days and inoculated with a standard nematode culture by incorporating the inoculum into the top cm of soil in the pots. The plants are returned to the growth chamber for about two weeks at which time the pots are allowed to dry until the plants begin to wilt. The roots are shaken free of soil and the degree of galling (swelling) noted as compared to galling of untreated control

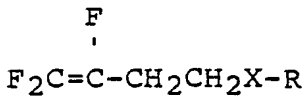
plants. The results are expressed as Knot Index and Percent Control as defined in the initial root-knot nematode activity tests reported above in Table 2. Table 8 appended reports the test results. The data indicate that many of the compounds exhibited good systemic nematicidal activity at the application rates tested as compared with untreated plants wherein no nematicidal activity was evident. Systemic nematicidal activity of any substantial degree is highly unusual and desirable and is not available from any commercial nematicides.

9. C. Elegans Nematode Screening Test and Evaluation

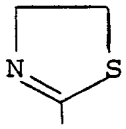
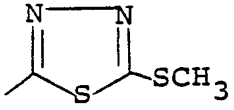
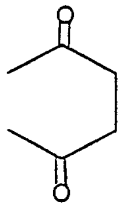
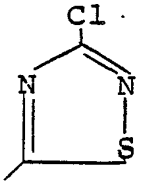
This in-vitro test using the free-living nematode Caenorhabditis elegans, is a modification of the assay developed by Simpkin and Coles, J. Chem. Tech. Tiotechnol, 31:66-69 (1981). In this test, nematicidal activity is evaluated by placing a suspension of C. elegans nematodes in a medium containing a food source (E. coli) and a candidate nematicide at test rates of 5.0-0.156 ppm. One milliliter of a test medium consisting of 5 mg ampicillin, 10,000 units of mycostatin and 10 ml of a dense suspension of Escherichia coli per 100 ml of a buffer solution, was pipetted into each well of a 24-well microtiter plate. The candidate nematicide, suspended at the appropriate concentration in dimethylsulfoxide, was added to the wells in 2.5 l volumes. Each rate of application was replicated two to three times. After thorough mixing of the contents of each well, 50 to 100 l of a nematode suspension in a buffer was added so that each well received 10-15 nematodes. After the nematodes were added, the microtiter plates were incubated at 20°C for 5-6 days.

The effect of the candidate nematicide on the survival and the reproduction of C. elegans was then evaluated by comparison of the level of population developed in the treated wells with that in untreated wells. Specific effects on population development, such as reduced egg hatch or molting disruption, were noted if they were evident. Tables 9 and 10 appended show high activity test results for many compounds of the invention at the application rates tested.

Table 1



$F_2C=C-CH_2CH_2X-R$

Cmpd. No.	X	R	Empirical Formula
1	S		$C_7H_8F_3NS_2$
2	S		$C_7H_7F_3N_2S_3$
3	O	$C(O)CF_2CF_2CF_3$	$C_8H_4F_{10}O_2$
4	O	4-chlorobenzoyl	$C_{11}H_8ClF_3O_2$
5	N		$C_8H_8F_3NO_2$
6	N	=C=S	$C_5H_4F_3NS$
7	CH_2	OH	$C_5H_7F_3O$
8	S		$C_6H_4ClF_3N_2S_2$

1155W30113Wjd-1

Table 1 (Continued)

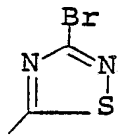
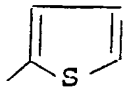
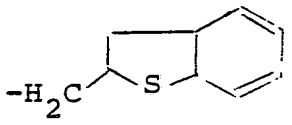
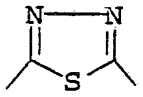
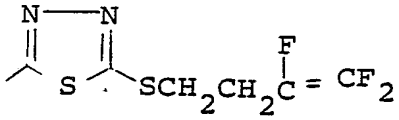
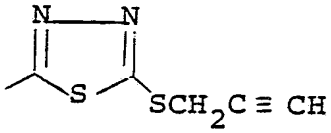
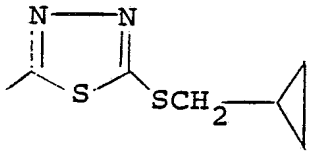
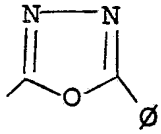
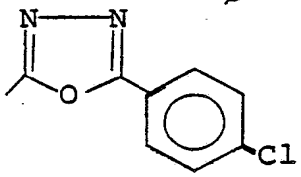
Cmpd. No.	X	R	Empirical Formula
9	S		$C_6H_4BrF_3N_2S_2$
10	S		$C_8H_7F_3S_2$
11	S		$C_{13}H_{11}F_3S_2$
12	S	 $SC(CH_3)_2CH_2C(CH_3)_3$	$C_{14}H_{21}F_3N_2S_3$
13	S		$C_{10}H_{18}F_6N_2S_3$
14	S		$C_9H_7F_3N_2S_3$
15	S		$C_9H_9F_3N_2S_3$
16	S		$C_{12}H_9F_3N_2OS$
17	S		$C_{12}H_8ClF_3N_2OS$

Table 1 (Continued)

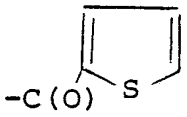
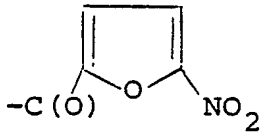
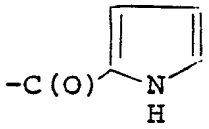
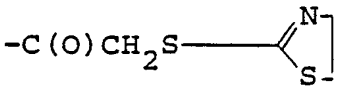
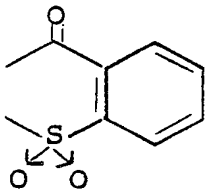
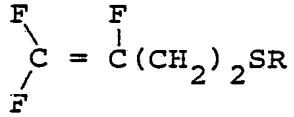
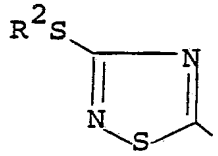
Cmpd. No.	X	R	Empirical Formula
18	S	$-CH_2CO_2CH_2CH_2C(F)=CF_2$	$C_{10}H_{10}F_6O_2S$
19	O	$-C(O)CF_2CF_3 \cdot (CH_3CH_2)_2O$	$C_{11}H_{14}F_8O_3$
20	O		$C_9H_6F_3NO_5$
21	O		$C_9H_6F_3NO_5$
22	O		$C_9H_7F_3NO_2$
23	O		$C_9H_{10}F_3NO_2S_2$
24	N		$C_{11}H_8F_3NO_3S$

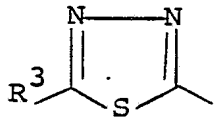
Table 1a



wherein:

R is 

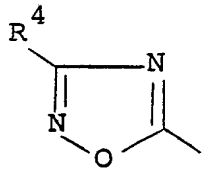
Compound No.	R^2	Empirical Formula M.P. (°C)
25	$-CH_2CH_2CF=CF_2$	$C_{10}H_8F_6N_2S_3$ liquid
26	4-nitrophenylmethyl	$C_{13}H_{10}F_3N_3O_2S_3$ liquid

R is 

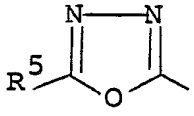
	R^3	
27	$-SCH_2CH_2F$	$C_8H_8F_4N_2S_3$ liquid
28	$-SCH_2CH_2C\equiv N$	$C_9H_8F_3N_3S_3$ liquid
29	$-SC_3H_7$	$C_9H_{11}F_3N_2S_3$ liquid
30	$-SCH(CH_3)_2$	$C_9H_{11}F_3N_2S_3$ liquid
31	$-SCH_2CH=CH_2$	$C_9H_9F_3N_2S_3$ liquid
32	$-SCH_2\phi$	$C_{13}H_{11}F_3N_2S_3$ liquid
33	$-SCH_2\phi$, 4-bromo	$C_{13}H_{10}BrF_3N_2S_3$ S (49-51)

Table 1a (Continued)

Compound No.	R^3	Empirical Formula M.P. (°C)
34	$-SCH_2\phi$, 2-fluoro	$C_{13}H_{10}F_4N_2S_3$ liquid
35	$-SCH_2\phi$, 4-nitro	$C_{13}H_{10}F_3N_3O_2S_3$ liquid
36	2-thienylmethylthio	$C_{11}H_9F_3N_2S_4$ liquid
37	$-\phi$,4-chloro	$C_{12}H_8ClF_3N_2S_2$ S (68-69)

R is 

	R^4	
38	$-CH_2\phi$, 4-fluoro	$C_{13}H_{10}F_4N_2OS$ liquid
39	$-\phi$, 4-chloro	$C_{12}H_8ClF_3N_2OS$ S (49-52)
40	$-\phi$, 4-nitro	$C_{12}H_8F_3N_3O_3S$ S (61-64)

R is 

	R^5	
41	$-C_3H_7$	$C_9H_{11}F_3N_2OS$ liquid
42	$-CH_2\phi$	$C_{13}H_{11}F_3N_2OS$ liquid
43	$-CH_2\phi$, 4-chloro	$C_{13}H_{10}ClF_3N_2OS$ liquid

Table 1a (Continued)

Compound No.	R^5	Empirical Formula M.P. (°C)
44	$-CH_2\phi$, 2-fluoro	$C_{13}H_{10}F_4N_2OS$ liquid
45	$-CH_2\phi$, 4-fluoro	$C_{13}H_{10}F_4N_2OS$ liquid
46	$-CH_2\phi$, 2,4-difluoro	$C_{13}H_9F_5N_2OS$ liquid
47	$-CH_2CH_2\phi$	$C_{14}H_{13}F_3N_2OS$ liquid
48	$-\phi$, 3-chloro	$C_{12}H_8ClF_3N_2OS$ S (55)
49	$-\phi$, 4-bromo	$C_{12}H_8BrF_3N_2OS$ S (58-61)
50	$-\phi$, 4-fluoro	$C_{12}H_8F_4N_2OS$ S (56-59)

Table 1b

Cmpd. No.	Name
1	2-(3,4,4-trifluoro-3-butenylthio)-4,5-dihydrothiazole
2	2-methylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
3	(3,4,4-trifluoro-3-butenyl) heptafluorobutyrate
4	(3,4,4-trifluoro-3-butenyl) 4-chlorobenzoate
5	N-(3,4,4-trifluoro-3-butenyl)succinimide
6	(3,4,4-trifluoro-3-butenyl) isothiocyanate
7	4,5,5-trifluoro-4-penten-1-ol
8	3-chloro-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole
9	3-bromo-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole
10	2-(3,4,4-trifluoro-3-butenylthio)thiophène
11	2-(3,4,4-trifluoro-3-butenylthiomethyl)-thianaphthene
12	2-(1,1,3,3-tetramethylbutylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
13	2,5-di(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
14	2-propargylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
15	2-cyclopropylmethylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
16	2-phenyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
17	2-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
18	(3,4,4-trifluoro-3-butenyl) (3,4,4-trifluoro-3-butenylthio)acetate

Table 1b (Continued)

Cmpd. No.	Name
19	(3,4,4-trifluoro-3-butenyl) pentafluoro-propionate, mono diethyl etherate
20	(3,4,4-trifluoro-3-butenyl) 2-thiophene-carboxylate
21	(3,4,4-trifluoro-3-butenyl) 5-nitro-2-furancarboxylate
22	(3,4,4-trifluoro-3-butenyl) 2-pyrrolecar-boxylate
23	(3,4,4-trifluoro-3-butenyl) [2-(4,5-di-hydrothiazolyl)thio]acetate
24	N-(3,4,4-trifluoro-3-butenyl)saccharine
25	3,5-di(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole
26	3-(4-nitrophenylmethylthio)-5-(3,4,4-tri-fluoro-3-butenylthio)-1,2,4-thiadiazole
27	2-(2-fluoroethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
28	2-(2-cyanoethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
29	2-propylthio-5-(3,4,4-trifluoro-3-butenyl-thio)-1,3,4-thiadiazole
30	2-(1-methylethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
31	2-(2-propenylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
32	2-phenylmethylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
33	2-(4-bromophenylmethylthio)-5-(3,4,4-tri-fluoro-3-butenylthio)-1,3,4-thiadiazole
34	2-(2-fluorophenylmethylthio)-5-(3,4,4-tri-fluoro-3-butenylthio)-1,3,4-thiadiazole

Table 1b (Continued)

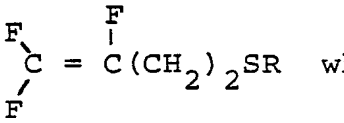
Cmpd. No.	Name
35	2-(4-nitrophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
36	2-(2-thienylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
37	2-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole
38	3-(4-fluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole
39	3-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole
40	3-(4-nitrophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole
41	2-propyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
42	2-phenylmethyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
43	2-(4-chlorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
44	2-(2-fluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
45	2-(4-fluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
46	2-(2,4-difluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
47	2-(2-phenylethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
48	2-(3-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
49	2-(4-bromophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole
50	2-(4-fluorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole

Table 1b (Continued)

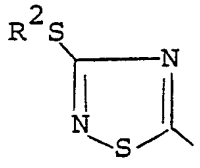
Cmpd. No.	Name
230	2-(3,4,4-trifluoro-3-butenylthio)thiazole
231	2-(2,3,3-trifluoro-2-propenylthio)thiazole
232	2-(4,4-difluoro-3-butenylthio)thiazole
233	2-(3,3-difluoro-2-propenylthio)thiazole
234	2-(4,4-dichloro-3-butenylthio)thiazole
235	2-(3,3-dichloro-2-propenylthio)thiazole
236	2-(4,4-dibromo-3-butenylthio)thiazole
237	2-(3,3-dibromo-2-propenylthio)thiazole
238	2-(2,3,3-trichloro-2-propenylthio)thiazole
239	2-(3,4,4-trichloro-3-butenylthio)thiazole
240	2-(2,3,3-tribromo-2-propenylthio)thiazole
241	2-(3,4,4-tribromo-3-butenylthio)thiazole

Table 1c

Substituted Thiadiazolyl/Oxadiazolyl Compounds



wherein:

R is 

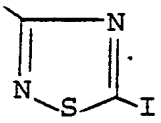
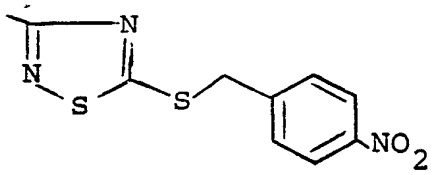
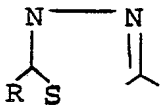
Compound No.	R^2	M.P. (°C)
51	phenylmethyl-	liquid
52	4-chlorophenylmethyl-	liquid
53	4-chlorophenylthiomethyl-	liquid
54	R is 	liquid
55	R is 	liquid

Table 1c (Continued)



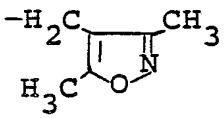
Compound No.	R^3	M.P. (°C)
56	4-chlorophenylmethyl-	liquid
57	$-SCH_2CH_3$	liquid
58	$-SCH_2CF_3$	liquid
59	$-SC_4H_9$	liquid
60	$-SCH(CH_3)C_2H_5$	liquid
61	$-SCH_2CH(CH_3)_2$	liquid
62	$-S(CH_2)_2CClFCBrF_2$	liquid
63	$-S(CH_2)_7CH_3$	liquid
64	$-S(CH_2)_{10}CH_3$	liquid
65	$-S(CH_2)_2CH=CH_2$	liquid
66	$-SCH(CH_3)CH=CH_2$	liquid
67	$-SCH_2C(CH_3)=CH_2$	liquid
68	$-SCH_2CH=CHCH_3$	liquid
69	$-S(CH_2)_3CH=CH_2$	liquid
70	$-SCH_2CH=C(CH_3)_2$	liquid
71	$-SCH_2C(Cl)=CH_2$	liquid
72	$-SCH_2C(Br)=CH_2$	liquid
73	$-SCH_2CH=C(Br)_2$	liquid
74	$-S(CH_2)_2CH=C(Cl)-$	solid (55°)
75	$-SCH_2C\equiv N$	solid (69°)
76	$-S(CH_2)_3C\equiv N$	liquid
77	$-S(CH_2)_4C\equiv N$	liquid
78		liquid
79	2,4-dimethylphenoxymethyl-	liquid
80	3-chlorophenylmethylthio-	liquid
81	4-chlorophenylmethylthio-	solid (38°)

Table 1c (Continued

Compound No.	R^3	M.P. (°C)
82	3,4-dichlorophenylmethylthio-	liquid
83	2,6-dichlorophenylmethylthio-	liquid
84	2-bromophenylmethylthio-	liquid
85	3-bromophenylmethylthio-	liquid
86	3,5-dibromophenylmethylthio-	liquid
87	3-fluorophenylmethylthio-	liquid
88	4-fluorophenylmethylthio-	liquid
89	2,4-difluorophenylmethylthio-	liquid
90	2,5-difluorophenylmethylthio-	liquid
91	3,4-difluorophenylmethylthio-	liquid
92	2,6-difluorophenylmethylthio-	liquid
93	2,3,4,5,6-pentafluorophenylmethylthio-	liquid
94	2-chloro-6-fluorophenylmethylthio-	liquid
95	2-iodophenylmethylthio-	liquid
96	2-methylphenylmethylthio-	liquid
97	3-methylphenylmethylthio-	liquid
98	2-trifluoromethylphenylmethylthio-	liquid
99	3-trifluoromethylphenylmethylthio-	liquid
100	4-trifluoromethylphenylmethylthio-	liquid
101	3-methoxyphenylmethylthio-	liquid
102	4-methoxyphenylmethylthio-	solid (42-44°)
103	4-trifluoromethoxyphenylmethylthio-	liquid
104	2-cyanophenylmethylthio-	liquid
105	3-cyanophenylmethylthio-	liquid
106	4-cyanophenylmethylthio-	solid (51-57°)
107	2-nitrophenylmethylthio-	liquid
108	3-nitrophenylmethylthio-	liquid
109	2-chloro-4-nitrophenylmethylthio-	liquid
110	4-chloro-2-nitrophenylmethylthio-	liquid
111	2-fluoro-4-nitrophenylmethylthio-	liquid
112	2-methyl-3-nitrophenylmethylthio-	liquid

Table 1c (Continued

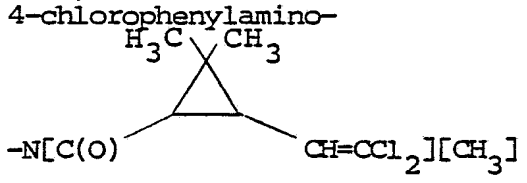
Compound No.	R^3	M.P. (°C)
113	2-nitro-5-methylphenylmethylthio-	liquid
114	2-methoxy-5-nitrophenylmethylthio-	liquid
115	3,5-dinitrophenylmethylthio-	liquid
116	4-phenylphenylmethylthio-	solid (62°)
117	2-methyl-3-phenylphenylmethylthio-	solid
118	anthracine-9-ylmethylthio-	liquid
119	5-chlorothien-2-ylmethylthio-	liquid
120	2-methylthiazol-4-ylmethylthio-	liquid
121	2,6-dichloropyridin-4-ylmethylthio-	liquid
122	1,3-benzodioxol-5-ylmethylthio-	liquid
123	phenylthiomethylthio-	liquid
124	1-phenylethylthio-	liquid
125	2-(4-nitrophenyl)ethylthio-	liquid
126	3-phenoxypropylthio-	liquid
127	$-N[C(O)CF_3][C_2H_5]$	liquid
128	$-N[C(O)CH_3][CH_3]$	liquid
129	$-N[C(O)CH_3]$[4-trifluoromethylphenyl]	solid
130	1,2-bis(4-chlorophenyl)urea-	solid
131	$-N[C(O)CF_3]$[4-methoxyphenyl]	solid
132	4-trifluoromethylphenylamino-	solid
133	4-methoxyphenylamino-	solid
134	4-chlorophenylamino-	solid
135		liquid
136	1-(4-trifluoromethylphenyl)-2-(4-chlorophenyl)urea-	solid
137	1-methyl-2-(4-chlorophenyl)urea-	solid (141-2°)

Table 1c (Continued)

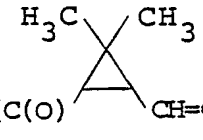
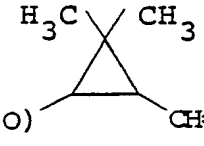
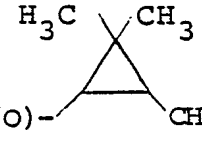
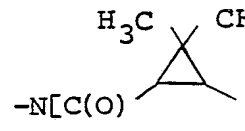
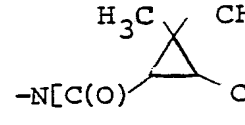
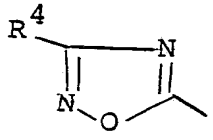
Compound No.	R^3	M.P. (°C)
138	-N[C(O)CH_3][4-chlorophenyl]	solid (84-85°)
139	-N[C(O)CH_3][4-fluorophenyl]	solid (96-97°)
140	 -N[C(O)- $CH=CCl_2$][4-methoxyphenyl]	liquid
141	4-nitrophenylamino-	solid
142	1-ethyl-2-(4-chlorophenyl)urea-	solid
143	-N[C(O)CH_3][4-methoxyphenyl]	solid
144	1-(4-fluorophenyl)-2-(4-chlorophenyl)-urea	solid
145	-NHC_2H_5	solid
146	4-fluorophenylamino-	solid
147	-N[CH_3][2,4-dichlorophenylmethylcarbonyl]	liquid
148	 -N[C(O)- $CH=CCl_2$][C_2H_5]	liquid
149	4-bromophenylamino-	solid
150	 -N[C(O)- $CH=CCl_2$][4-trifluoromethylphenyl]	liquid
151	-N[C_2H_5][phenylmethoxycarbonyl]	solid
152	-N[C(O)CH_3][C_2H_5]	liquid
153	bromomethylthio-	liquid
154	-N[C(O)CH_3][4-bromophenyl]	solid

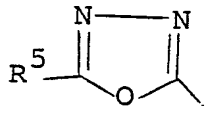
Table 1c (Continued)

Compound No.	R^3	M.P. (°C)
155		solid
156		liquid
157	$-S(CH_2)_3CH_2Cl$	semi-solid
158	$-SCH_2Cl$	liquid
159	$-S(CH_2)_4Cl$	lqiuid
160	$-S(CH_2)_2CH_2Cl$	liquid
161	$-S(CH_2)_3CH_2Br$	solid (67-69°)

R is 

Compound No.	R^4	M.P. (°C)
162	4-chlorophenylmethyl-	liquid
163	4-methylphenyl-	liquid
164	phenylmethyl-	liquid
165	phenyl-	liquid
166	2-chlorophenyl-	liquid

Compound No.	R^4	M.P. (°C)
167	3-chlorophenyl-	solid (48-51°)
168	3-trifluoromethylphenyl-	solid (41-44°)
169	4-methoxyphenylmethyl-	liquid
170	3-nitrophenyl-	solid (69-71°)

R is 

Compound No.	R^5	M.P. (°C)
171	$-CH_3$	liquid
172	$-C_2H_5$	liquid
173	$-CH(CH_3)_2$	liquid
174	$-CH_2CH(CH_3)_2$	liquid
175	$-C(CH_3)_3$	liquid
176	$-(CH_2)_4CH_3$	liquid
177	$-(CH_2)_{16}CH_3$	solid (45°)
178	$-C\equiv C(CH_2)_4CH_3$	liquid
179	$-CH_2CH(CH_3)CF_3$	liquid
180	2-chlorophenylmethyl-	liquid
181	2-bromophenylmethyl-	liquid
182	4-bromophenylmethyl-	solid (38-40°)
183	2-methylphenylmethyl-	liquid
184	3-methylphenylmethyl-	liquid
185	2-bromo-4,5-dimethoxyphenylmethyl-	solid (54-59°)
186	2-nitrophenylmethyl-	liquid
187	4-nitrophenylmethyl-	liquid
188	thien-2-ylmethyl-	liquid
189	1,4-benzodioxan-6-ylmethyl-	liquid

Table 1c (Continued)

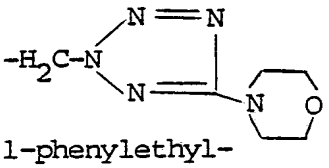
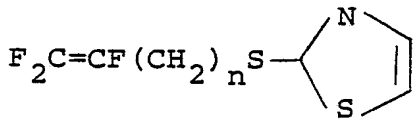
Compound No.	R^5	M.P. (°C)
190	1,3-benzodioxol-5-ylmethyl-	solid (69-71°)
191		liquid
192	1-phenylethyl-	liquid
193	2-(4-nitrophenyl)ethyl-	liquid
194	2-(4-chlorophenyl)ethenyl-	liquid
195	2-(4-bromophenyl)ethenyl-	liquid
196	2-(2-fluorophenyl)ethenyl-	liquid
197	3-phenylpropyl-	liquid
198	4-phenylbutyl-	liquid
199	4-chlorophenoxymethyl-	liquid
200	4-methylphenoxymethyl-	liquid
201	3-methyl-4-chlorophenoxymethyl-	liquid
202	4-nitrophenoxymethyl-	liquid
203	1-(4-chlorophenoxy)ethyl-	liquid
204	1-(4-methylphenoxy)ethyl-	liquid
205	2-(4-chlorophenylthio)ethyl-	solid (54-59°)
206	1-(4-chlorophenoxy)propyl-	liquid
207	2-chlorophenyl-	liquid
208	2-bromophenyl-	liquid
209	2,5-dichlorophenyl-	liquid
210	4-(1-methylethyl)phenyl-	liquid
211	2-methoxyphenyl-	liquid
212	3-methoxyphenyl-	liquid
213	4-methoxyphenyl-	liquid
214	3,4-dimethoxyphenyl-	solid (51°)
215	4-nitrophenyl-	solid (94-96°)
216	2-aminophenyl-	solid (57-61°)
217	4-hydroxyphenyl-	solid (96-101°)

Table 1c (Continued)

Compound No.	R^5	M.P. (°C)
218	4-acetyloxyphenyl-	solid (63-66°)
219	4-(methylaminocarbonyloxy)phenyl-	solid (108-111°)
220	4-phenylphenyl-	solid (49-52°)
221	naphth-2-yl-	solid (70-72°)
222	naphth-1-yl-	solid (68°)
223	thien-2-yl-	liquid
224	furan-2-yl-	liquid
225	4-methyl-1,2,3-thiadiazol-5-yl-	liquid
226	2-(4-chlorophenyl)ethyl-	solid (43-45°)
227	2-(2-chlorophenyl)ethyl-	liquid
228	2-(4-fluorophenyl)ethyl-	liquid
229	phenylmethyl	liquid

Table 1d (Continued)

Polyhaloalkenylthio Thiazolyl Compounds



Compound No.	n	M.P. (°C)
230	2	liquid
231	1	liquid

Table 2

Initial Activity Against the Root-knot Nematode

Compound No.	Application Rate (ppm)	Percent Control
1	10.0	100
	5.0	99
	2.5	99
	5.0	100
	2.5	100
	1.25	99
	0.625	100
	0.313	99
	0.625	100
	0.313	98
	0.156	95
	0.078	56
2	10.0	100
	5.0	96
	2.5	96
	5.0	99
	2.5	95
	1.25	86
	0.625	84
	0.313	38
3	10.0	95
	5.0	83
	2.5	71
4	2.5	99
	1.25	56
	0.625	44
	0.313	38
5	2.5	81
	1.25	70
	0.625	6
	0.313	0
6	10.0	100
	5.0	78
	2.5	38
7	10.0	79
	5.0	44
	2.5	25

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
8	2.5	100
	1.25	100
	0.625	100
	0.312	100
	0.625	100
	0.312	98
	0.156	95
	0.078	58
10	5.0	99
	2.5	95
	1.25	81
	0.625	63
11	5.0	83
	2.5	78
	1.25	67
	0.625	0
12	2.5	100
	1.25	79
	0.625	69
	0.313	8
13	2.5	99
	1.25	99
	0.625	96
	0.313	71
	0.625	95
	0.313	79
	0.156	13
	0.078	0
14	2.5	83
	1.25	25
	0.625	0
	0.313	0
15	2.5	100
	1.25	97
	0.625	31
	0.313	6

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
16	2.5	95
	1.25	44
	0.625	25
	0.313	0
17	10.0	100
	5.0	100
	2.5	100
18	10.0	100
	5.0	99
	2.5	96
	5.0	80
	2.5	69
	1.25	38
	0.625	19
	0.313	0
19	10.0	69
	5.0	75
	2.5	58
20	2.5	98
	1.25	63
	0.625	6
	0.313	0
21	2.5	64
	1.25	31
	0.625	8
	0.313	0
22	2.5	96
	1.25	44
	0.625	0
	0.313	0
23	10.0	96
	5.0	84
	2.5	76
24	10.0	78
	5.0	63
	2.5	19

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
25	2.5	99
	1.25	97
	.625	97
	.312	78
26	2.5	86
	1.25	63
	.625	0
	.312	0
27	2.5	100
	1.25	99
	.625	79
	.312	31
28	2.5	100
	1.25	98
	.625	86
	.312	81
29	2.5	99
	1.25	99
	.625	99
	.312	95
30	2.5	100
	1.25	99
	.625	99
	.312	97
31	2.5	99
	1.25	96
	.625	78
	.312	69
	.625	63
	.312	44
	.156	13
	.078	0
32	2.5	100
	1.25	99
	.625	97
	.312	78

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
32 cont'd	.625	98
	.312	69
	.156	31
	.078	8
33	2.5	97
	1.25	84
	.625	70
	.312	38
34	2.5	100
	1.25	99
	.625	99
	.312	86
	.625	99
	.312	86
	.156	64
	.078	38
35	2.5	100
	1.25	98
	.625	70
	.312	67
	.625	97
	.312	51
	.156	6
	.078	0
35	2.5	100
	1.25	99
	.625	96
	.312	69
	.625	99
	.312	71
	.156	25
	.078	0
37	.625	0
	.312	0
	.156	0
	.078	0

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
38	2.5	98
	1.25	96
	.625	76
	.312	63
39	2.5	100
	1.25	98
	.625	84
	.312	19
	2.5	100
	1.25	99
	.625	83
	.312	19
40	2.5	99
	1.25	84
	.625	56
	.312	0
41	2.5	100
	1.25	100
	.625	98
	.312	76
	.625	100
	.312	97
	.156	84
	.078	31
42	2.5	100
	1.25	98
	.625	98
	.312	86
	.625	96
	.312	83
	.156	50
	.078	38
43	.625	99
	.312	78
	.156	38
	.078	13

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
43 cont'd	.5	99
	2.5	97
	1.25	56
	.625	13
44	2.5	98
	1.25	86
	.625	76
	.312	50
45	2.5	99
	1.25	99
	.625	99
	.312	95
46	2.5	99
	1.25	98
	.625	98
	.312	85
47	2.5	100
	1.25	96
	.625	95
	.312	95
48	2.5	98
	1.25	95
	.625	78
	.312	64
	.625	87
	.312	56
	.156	38
	.078	6
49	2.5	100
	1.25	100
	.625	100
	.312	98
50	2.5	100
	1.25	99
	.625	99
	.312	78

Table 2 (Continued)

Compound No.	Application Rate (ppm)	Percent Control
230	2.5	100
	1.25	100
	0.625	81
	0.313	44

Table 3

Residual Activity Against the Root-knot Nematode

Cmpd. No.	Application Rate (ppm)	Inoculation, Weeks After Treatment	Percent Control
1	10	1	98
		2	44
		4	0
	10	1	99
		2	75
		4	42
	5	1	99
		2	63
		4	25
2	10	1	77
		2	56
		4	69
	10	1	96
		2	38
		4	50
	5	1	98
		2	38
		4	42
8	5	1	-
		2	-
		4	98
13	10	1	99
		2	99
		4	95
	5	1	98
		2	98
		4	75
18	10	1	0
		2	0
		4	0
21	5	1	13
		2	8
		4	0

Table 3a

Residual Activity Against The Root-Knot Nematode
- 5% Dust - Application Rate: 5 ppm

Compound No.	Inoculation Post-Treatment	Percent Control
25	1 Week	100
	2 Weeks	97
	4 Weeks	98
27	1 Week	99
	2 Weeks	97
	4 Weeks	99
28	1 Week	100
	2 Weeks	100
	4 Weeks	8
29	1 Week	100
	2 Weeks	98
	4 Weeks	81
30	1 Week	98
	2 Weeks	97
	4 Weeks	83
31	1 Week	97
	2 Weeks	97
	4 Weeks	95
32	1 Week	99
	2 Weeks	99
	4 Weeks	82
	1 Week	99
	2 Weeks	99
	4 Weeks	98
35	1 Week	99
	2 Weeks	96
	4 Weeks	84
36	1 Week	98
	2 Weeks	99
	4 Weeks	95

Table 3a (Continued)

Compound No.	Inoculation Post-Treatment	Percent Control
41	1 Week	97
	2 Weeks	63
	4 Weeks	6
42	1 Week	99
	2 Weeks	97
	4 Weeks	0
43	1 Week	100
	2 Weeks	100
	4 Weeks	100
44	1 Week	100
	2 Weeks	100
	4 Weeks	100
45	1 Week	99
	2 Weeks	100
	4 Weeks	98
46	1 Week	99
	2 Weeks	100
	4 Weeks	99
47	1 Week	96
	2 Weeks	25
	4 Weeks	0
48	1 Week	97
	2 Weeks	97
	4 Weeks	69

Table 4

Initial Activity Against the Stunt Nematode

Compound. No.	Rate of Application (ppm)	Percent Control
1	10	61
	5	30
2	5	72
6	5	51

Table 4a

Initial Activity Against the Stunt Nematode

Application rate: 5 ppm

Compound No.	Percent Control	Compound No.	Percent Control
25	89	41	29
	56	42	76*
27	62		33
28	38	43	81
29	56		76
30	66		62
31	52	44	75
32	84	45	80*
33	52	46	65*
34	88	47	35
	56	48	82
35	77		66
	83	49	58
36	64	50	53
	91		

*Some phytotoxicity

Table 5

Initial Activity Against the Lesion Nematode

Compound No.	Rate of Application (ppm)	Percent Control
1	5	82
	5	52
	2.5	0
2	5	0
10	2.5	33
18	5	0
21	2.5	54
25	2.5	77
	2.5	79
27	2.5	63
28	2.5	45
29	2.5	68
30	2.5	75
31	2.5	11
32	2.5	28
	2.5	15
	1.25	0
	.625	0
33	2.5	46
34	2.5	52
	2.5	58
	2.5	55
35	2.5	52
	2.5	78

Table 5 (Continued)

Compound No.	Rate of Application (ppm)	Percent Control
36	2.5	59
	2.5	19
	1.25	2
	.625	0
	2.5	71
41	2.5	64
42	2.5	73
		82
43	2.5	93
	2.5	78
44	2.5	88
45	2.5	41
46	2.5	77
47	2.5	69
48	2.5	85
	2.5	78

Table 6

Initial Activity Against the Cyst Nematode

Compound No.	Rate of Application (ppm)	Percent Control
1	5	94
	5	79[1]
2	5	70
8	5	92
18	5	8
21	2.5	33
25	5	83
27	5	57
31	5	7
32	5	16
	5	78
35	5	0
36	5	37
41	5	0
42	5	30
44	5	59
48	5	86

[1]Whole cysts rather than homogenized cysts were used.

Table 7

Soil Mobility Evaluations Against the Root-knot Nematode

Cmpd. No.	Application Rate (ppm)	Location of Test Container	Percent Control
1	30	Top	97
		Middle	95
		Bottom	85
	10	1 (Top)	100
		2	100
		3	100
		4	99
		5	97
		6 (Bottom)	42
	5	Top	100
		Middle	98
		Bottom	99
	2.5	Top	100
		Middle	100
		Bottom	100
	1.25	Top	100
		Middle	99
		Bottom	96
	0.625	Top	97
		Middle	98
		Bottom	77
	0.313	Top	77
		Middle	75
		Bottom	25
2	30	Top	42
		Middle	33
		Bottom	25
8	5	Top	100
		Middle	100
		Bottom	96
18	30	Top	33
		Middle	25
		Bottom	25
21	30	Top	100
		Middle	96
		Bottom	99

Table 7a

Soil Mobility Evaluations Against The Root-Knot Nematode - 5% Dust; Application Rate: 5 ppm

Compound No.	Location of Test Container	Percent Control
25	TOP	100
	MIDDLE	69
	BOTTOM	8
27	TOP	99
	MIDDLE	100
	BOTTOM	100
28	TOP	68
	MIDDLE	83
	BOTTOM	68
29	TOP	98
	MIDDLE	81
	BOTTOM	50
30	TOP	99
	MIDDLE	100
	BOTTOM	17
31	TOP	98
	MIDDLE	86
	BOTTOM	50
32	TOP	99
	MIDDLE	75
	BOTTOM	25
34	TOP	98
	MIDDLE	67
	BOTTOM	8
35	TOP	99
	MIDDLE	50
	BOTTOM	0
36	TOP	97
	MIDDLE	17
	BOTTOM	0
38	TOP	0
	MIDDLE	0
	BOTTOM	0

Table 7a (Continued)

Compound No.	Location of Test Container	Percent Control
41	TOP	97*
	MIDDLE	95*
	BOTTOM	8
42	TOP	100
	MIDDLE	100
	BOTTOM	100
43	TOP	99
	MIDDLE	97
	BOTTOM	81
44	TOP	100
	MIDDLE	100
	BOTTOM	96
45	TOP	98
	MIDDLE	97
	BOTTOM	83
46	TOP	96
	MIDDLE	97
	BOTTOM	78
47	TOP	98
	MIDDLE	96
	BOTTOM	58
48	TOP	50
	MIDDLE	0
	BOTTOM	0
	TOP	96*
	MIDDLE	75
	BOTTOM	42
49	TOP	99
	MIDDLE	71
	BOTTOM	8
50	TOP	98
	MIDDLE	71
	BOTTOM	33

*Some phytotoxicity

Table 8

Systemic Activity Against the Root-knot Nematodes

Cmpd. No.	Application Test Rate (ppm)	Percent Control
12	2000	73, 99
	1000	42, 95
13	2000	79
15	2000	83
16	2000	67
17	2000	42
31	2000	71
	1250	0
32	2000	25
33	2500	17
35	2000	0
36	2000	97
	1250	17
41	2000	17
48	2000	50
	2500	33

Table 10

Evaluations Against C. Elegans

Compound No.	Rate (PPM)	Percent Inhibition of Reproduction	Percent Mortality
25	5	100	100
	2.5	58	0
	1.25	17	0
26	5	100	100
	2.5	100	100
	1.25	100	100
32	5	100	8
	2.5	42	0
	1.25	25	0
33	5	100	100
	2.5	100	100
	1.25	100	100
34	5	100	100
	2.5	100	100
	1.25	0	0
35	5	100	100
	2.5	100	100
	1.25	100	100
37	5	100	100
	2.5	100	100
	1.25	100	100
39	5	100	100
	5	100	100
	2.5	100	100
	2.5	100	100
	1.25	100	67
	1.25	100	58
40	5	100	100
	2.5	100	100
	1.25	100	100
43	5	100	83
	2.5	100	67
	1.25	42	0
48	5	100	100
	2.5	25	0
	1.25	17	0

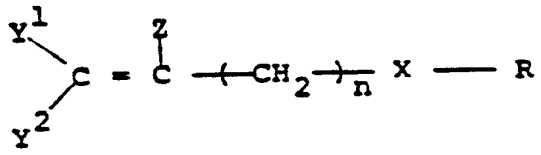
Table 9

Screen Against C. Elegans - Rate: 5 ppm

Compound No.	Percent Inhibition of Reproduction	Percent Mortality
25	100	75
26	100	100
27	38	0
31	38	0
32	100	100
33	100	100
34	100	25
35	100	100
37	100	100
39	100	100
43	100	25
44	25	0
45	25	0
48	100	88

Claims:

1. Polyhaloalkene compounds characterized by the formula:



wherein X is sulfur, oxygen, nitrogen or methylene, Y^1 and Y^2 independently are fluorine, chlorine or bromine, Z is hydrogen or the same as Y^1 or Y^2, and n is 1-4; provided that:

(A) when X is sulfur, R is thiazolyl, optionally substituted thienyl, optionally substituted thianaphthyl, optionally substituted thiazolinyl, optionally substituted thiadiazolyl, optionally substituted oxadiazolyl or 3,4,4-trifluoro-3-butenyloxycarbonylmethyl;

(B) when X is oxygen, R is $C(O)R^1$ wherein R^1 is perfluoroalkyl, optionally substituted phenyl, optionally substituted thienyl, optionally substituted furanyl, optionally substituted pyrrolyl or dihydrothiazolylthiomethyl;

(C) when X is nitrogen, R taken with the nitrogen is an isothiocyanate, succinimide or saccharine group; and

(D) when X is methylene, R is hydroxy.

2. Compounds of the formula of claim 1 characterized in that X is sulfur.

3. Compounds of the formula of claim 1 characterized in that X is sulfur and R is a thiazolyl group.

4. A compound of claim 3 which is 2-(3,4,4-trifluoro-3-butenylthio)thiazole or 2-(2,3,3-trifluoro-2-propenylthio)thiazole.

5. Compounds of the formula of claim 1 characterized in that X is sulfur and R is a thiadiazolyl or an oxadiazolyl group, substituted on a nuclear carbon atom.

6. Substituted thiadiazolyl compounds of claim 5 characterized in that the substituent is R^2S- wherein R^2 is 3,4,4-trifluoro-3-butenyl, phenylmethyl optionally substituted with halogen or nitro, or phenylthiomethyl optionally substituted with halogen or nitro.

7. Substituted thiadiazolyl compounds of claim 3 characterized in that the substituent is iodo.

8. Substituted thiadiazolyl compounds of claim 5 characterized in that the substituent (R^3) is optionally substituted aryl, aralalkyl, aryloxyalkyl, alkylthio, haloalkylthio, cyanoalkylthio, arylalkylthio, aryloxyalkylthio, arylthioalkylthio, optionally substituted heterocycloalkylthio, alkenylthio, haloalkenylthio, halocycloalkylalkenylthio, or an amino group mono- or disubstituted with members independently selected from alkyl, alkylcarbonyl, haloalkylcarbonyl, optionally substituted aryl, arylaminocarbonyl, arylalkylcarbonyl, arylalkoxycarbonyl and 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarbonyl.

9. Substituted oxadiazolyl compounds of claim 5 characterized in that the substituent (R^4) is optionally substituted aryl or an arylalkyl group substituted with chloro, fluoro, alkyl, haloalkyl, alkoxy or nitro.

10. Substituted oxadiazolyl compounds of claim 5 characterized in that the substituent (R^5) is alkyl, haloalkyl, optionally substituted aryl, arylalkyl, aryloxyalkyl, arylthioalkyl, optionally substituted heterocycloalkyl, arylalkenyl or alkynyl.

11. Compounds of claim 2 selected from
2-(3,4,4-trifluoro-3-butenylthio)thiophene,
2-(3,4,4-trifluoro-3-butenylthio)-4,5-dihydrothiazole,
2-methylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(1,1,3,3-tetramethylbutylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2,5-di(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-cyclopropylmethylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
3-chloro-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole,
2-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,
3,5-di(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole,
3-(4-nitrophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-thiadiazole,
2-(2-fluoroethylthio)-3-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(2-cyanoethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-propylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(1-methylethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(2-propenylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-phenylmethylthio-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(4-bromophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,
2-(2-fluorophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,

2-(4-nitrophenylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,

2-(2-thienylmethylthio)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,

2-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-thiadiazole,

3-(4-fluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole,

3-(4-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole,

3-(4-nitrophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,2,4-oxadiazole,

2-propyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-phenylmethyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(4-chlorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(2-fluorophenylmethyl-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(4-fluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(2,4-difluorophenylmethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(2-phenylethyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(3-chlorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(4-bromophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole,

2-(4-fluorophenyl)-5-(3,4,4-trifluoro-3-butenylthio)-1,3,4-oxadiazole, 2-(3,4,4-trifluoro-3-butenylthio)thiazole and

2-(2,3,3-trifluoro-2-butenylthio)thiazole.

12. Compounds of the formula of claim 1 characterized in that X is oxygen.

13. Compounds of claim 12 selected from (3,4,4-trifluoro-3-butenyl) pentafluoropropionate mono diethyl etherate,

(3,4,4-trifluoro-3-butenyl) heptafluorobutyrate,

(3,4,4-trifluoro-3-butenyl) 4-chlorobenzoate.

(3,4,4-trifluoro-3-butenyl) 2-thiophenecarboxylate,

(3,4,4-trifluoro-3-butenyl) 5-nitro-2-furancarboxylate,

(3,4,4-trifluoro-3-butenyl) 2-pyrrolecarboxylate and

(3,4,4-trifluoro-3-butenyl) [2-(4,5-dihydrothiazolyl)thio]acetate.

14. Compounds of the formula of claim 1 characterized in that X is nitrogen.

15. Compounds of claim 14 selected from (3,4,4-trifluoro-3-butenyl) isothiocyanate,

N-(3,4,4-trifluoro-3-butenyl)succinimide and

N-(3,4,4-trifluoro-3-butenyl)saccharine.

16. Compounds of the formula of claim 1 characterized in that X is methylene.

17. A compound of claim 16 which is 4,5,5-trifluoro-4-penten-1-ol.

18. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 1.

19. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 2.

20. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 3.

21. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 4.

22. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 5.

23. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 6.

24. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 8.

25. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 9.

26. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 10.

27. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of at least one compound of claim 11.

28. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 12.

29. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 13.

30. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 14.

31. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 15.

32. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 16.

33. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 17.

34. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 1 in an agriculturally acceptable carrier.

35. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 2 in an agriculturally acceptable carrier.

36. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 3 in an agriculturally acceptable carrier.

37. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 4 in an agriculturally acceptable carrier.

38. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 5 in an agriculturally acceptable carrier.

39. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 6 in an agriculturally acceptable carrier.

40. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 8 in an agriculturally acceptable carrier.

41. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 9 in an agriculturally acceptable carrier.

42. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 10 in an agriculturally acceptable carrier.

43. A nematicidal composition characterized by a nematicidally effective amount of at least one compound of claim 11 in an agriculturally acceptable carrier.

44. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 12 in an agriculturally acceptable carrier.

45. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 13 in an agriculturally acceptable carrier.

46. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 14 in an agriculturally acceptable carrier.

47. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 15 in an agriculturally acceptable carrier.

48. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 16 in an agriculturally acceptable carrier.

49. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 17 in an agriculturally acceptable carrier.

50. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 1.

51. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 2.

52. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 3.

53. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 4.

54. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 5.

55. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 6.

56. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 8.

57. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 9.

58. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 10.

59. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 11.

60. An anthelmintic composition characterized by an effective amount of a compound of claim 1 in combination with a pharmaceutically acceptable carrier.

61. An anthelmintic composition characterized by an effective amount of a compound of claim 2 in combination with a pharmaceutically acceptable carrier.

62. An anthelmintic composition characterized by an effective amount of a compound of claim 3 in combination with a pharmaceutically acceptable carrier.

63. An anthelmintic composition characterized by an effective amount of a compound of claim 4 in combination with a pharmaceutically acceptable carrier.

64. An anthelmintic composition characterized by an effective amount of a compound of claim 5 in combination with a pharmaceutically acceptable carrier.

65. An anthelmintic composition characterized by an effective amount of a compound of claim 6 in combination with a pharmaceutically acceptable carrier.

66. An anthelmintic composition characterized by an effective amount of a compound of claim 8 in combination with a pharmaceutically acceptable carrier.

67. An anthelmintic composition characterized by an effective amount of a compound of claim 9 in combination with a pharmaceutically acceptable carrier.

68. An anthelmintic composition characterized by an effective amount of a compound of claim 10 in combination with a pharmaceutically acceptable carrier.

69. An anthelmintic composition characterized by an effective amount of a compound of claim 11 in combination with a pharmaceutically acceptable carrier.

AMENDED CLAIMS

[received by the International Bureau on 14 November 1986 (14.11.86) original claims 13,14, and 48,49 cancelled; claims 1,32,33 amended; other claims unchanged (4 pages)]

1. (Amended) Polyhaloalkene compounds characterized by the formula:

$$F_2C=CF(CH_2)_nXR$$

wherein X is sulfur, oxygen or nitrogen and n is 1-4; provided that:

(A) when X is sulfur, R is thiazolyl, optionally substituted thienyl, optionally substituted thianaphthyl, optionally substituted thiazolinyl, optionally substituted thiadiazolyl, optionally substituted oxadiazolyl or 3,4,4-trifluoro-3-butenyloxycarbonylmethyl;

(B) when X is oxygen, R is $C(O)R^1$ wherein R^1 is perfluoroalkyl, optionally substituted phenyl, optionally substituted thienyl, optionally substituted furanyl, optionally substituted pyrrolyl or dihydrothiazolylthiomethyl; and

(C) when X is nitrogen, R taken with the nitrogen is an isothiocyanate, succinimide or saccharine group.

2. Compounds of the formula of claim 1 characterized in that X is sulfur.

3. Compounds of the formula of claim 1 characterized in that X is sulfur and R is a thiazolyl group.

4. A compound of claim 3 which is 2-(3,4,4-trifluoro-3-butenylthio)thiazole or 2-(2,3,3-trifluoro-2-propenylthio)thiazole.

13. Compounds of claim 12 selected from (3,4,4-trifluoro-3-butenyl) pentafluoropropionate mono diethyl etherate,

(3,4,4-trifluoro-3-butenyl) heptafluorobutyrate,

(3,4,4-trifluoro-3-butenyl) 4-chlorobenzoate.

(3,4,4-trifluoro-3-butenyl) 2-thiophenecarboxylate,

(3,4,4-trifluoro-3-butenyl) 5-nitro-2-furancarboxylate,

(3,4,4-trifluoro-3-butenyl) 2-pyrrolecarboxylate and

(3,4,4-trifluoro-3-butenyl) [2-(4,5-dihydrothiazolyl)thio]acetate.

14. Compounds of the formula of claim 1 characterized in that X is nitrogen.

15. Compounds of claim 14 selected from (3,4,4-trifluoro-3-butenyl) isothiocyanate,

N-(3,4,4-trifluoro-3-butenyl)succinimide and

N-(3,4,4-trifluoro-3-butenyl)saccharine.

16. (Cancelled)

17. (Cancelled)

18. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 1.

19. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 2.

20. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 3.

30. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 14.

31. A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of claim 15.

32. (Amended) A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of the formula $F_2C=CF(CH_2)_nCH_2OH$ wherein n is 1-4.

33. (Amended) A method of controlling nematodes characterized by applying to the locus where control is desired a nematicidally effective amount of a compound of the formula $F_2C=CFCH_2CH_2CH_2OH$.

34. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 1 in an agriculturally acceptable carrier.

35. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 2 in an agriculturally acceptable carrier.

36. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 3 in an agriculturally acceptable carrier.

37. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 4 in an agriculturally acceptable carrier.

38. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 5 in an agriculturally acceptable carrier.

39. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 6 in an agriculturally acceptable carrier.

40. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 8 in an agriculturally acceptable carrier.

41. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 9 in an agriculturally acceptable carrier.

42. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 10 in an agriculturally acceptable carrier.

43. A nematicidal composition characterized by a nematicidally effective amount of at least one compound of claim 11 in an agriculturally acceptable carrier.

44. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 12 in an agriculturally acceptable carrier.

45. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 13 in an agriculturally acceptable carrier.

46. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 14 in an agriculturally acceptable carrier.

47. A nematicidal composition characterized by a nematicidally effective amount of a compound of claim 15 in an agriculturally acceptable carrier.

48. (Cancelled)

49. (Cancelled)

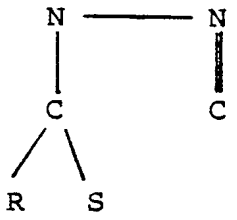
50. A method of controlling helminths that infect animals, characterized by administering to an animal an anthelmintic amount of a compound of claim 1.

STATEMENT UNDER ARTICLE 19

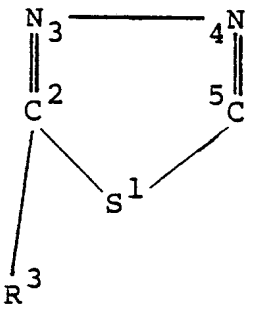
The amendments to the claims and abstract are presented herewith as retyped pages 81, 85, 87, 88, and 91. The amendments to claims 1 have limited the original claims to compounds represented by the Formula I in which Y^1, Y^2 and Z are only fluorine and X is sulfur, oxygen or nitrogen. In view of these changes the amendment replaces the structures arbitrary symbols Y^1, Y^2 and Z with F, the chemical symbol for fluorine. This amendment thus reduces the scope of the claims. The basis of the amendments are found in the specification; for example the structure on page 39 is the same as the amended structure of claim 1 and the compounds listed in Table 1 show compounds in which X is sulfur, oxygen or nitrogen.

The amendments to claims 32 and 33 make these amended claims consistent with the scope of amended claim 1 and eliminate their dependency on cancelled claims 16 and 17.

The Applicant has requested amendment of page 50 in order to correct the structure by supplying the missing bond between sulfur and carbon. The original structure



has been corrected to



A comparison of the structure and text at page 4, lines 7 to 11 et seq with the structure on original page 50 and the following tabular material makes it clear a bond between carbon and sulfur was omitted in the original structure. Thus, the correction of page 50 conforms the structure at page 50 to the structure at page 4, lines 7 to 11.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01284

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4) C07C 33/42, 69/63, 69/767; C07D 271/06 271/10 277/26 285/06, 285/12 See attachment

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	260/454; 548/129, 130,132,136,142,144,182,187,210, 531,545; 549/49, 62, 79,481,484;560/11,,219227;568/843 849:514/361,363,364,369,373,423, see attachment

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [6]

CHEMICAL ABSTRACTS 1-104

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3,058,990 (HARMUN) 16 October 1962 See entire document	1,2,5,6,8, 11,18,19,22 23,24,27,34, 35,38-40,43, 50,51,54-56, 59-61,64-66, 69
X	US, A, 3,080,405 (LARSEN 05 March 1963 See Ex. IX and column 8 line 74	1,12,13,34, 44, 60
X	EP, A, 138091 (DAIKIN) 24 April 1985 See Ex. 4	1,16,17,34, 48,49,60
X	US, A, 3,513,172 (BROKKE) 19 May 1970 See entire doucment	1-6,8,11,18-24,34-40,43, 50-56,59-66 69

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
05 September 1986	18 SEP 1986
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Robert Gerstl

Form PCT/ISA/210 (second sheet) (May 1986)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	US, A, 3,463,856 (KADO) 26 August 1969	1,14
X	Chemical Abstracts, Volume 93 No. 3, issued 21 July 1980 (Columbus, Ohio) Abstract No. 20617e. Yu v. Shcheglov "Herbicide Activity of Substances containing the triallyl group 2. Trichloroallyl esters of aliphatic carboxylic and halocarboxylic acids" Agrokhimiya (3) 97-101 (1980) Russ. See RN 73938-53-1	1,12,34,44, 60
X	FR, A, 1,528,170 (Agripat) 07 June 1968 See compound 2, Table III	1,2,4,34,35 38,60,61,65
X	JP, A, 49/8259 (Terakawa) 25 February 1974 See entire document	1,2,5,8,34, 35,38,40,60 61,64,66

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ....., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

See attachment

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

PCT/US86/01284

Attachment to 210

Part I.

IPC (4) AOIN 31/02, 37/02, 37/10, 43/78, 43/82

US.Cl. 260/454; 548/129, 130, 132, 136, 142, 144, 182, 187, 210, 531, 545

549/49, 62, 79, 481, 484

560/111, 219, 227

568/843; 849

514/361, 363, 364, 369, 373, 423, 425, 443, 445, 448, 514, 544, 549, 550, 739

Part II. 425, 443, 445, 448, 514, 544, 549, 550, 739

Part VI.

I. Compounds where X is sulfur classified in 548/129 -Claims 2-11, 19-27, 35-43, 51-59, 61-69.

II. Compounds where X is Oxygen classified in 548/187 -Claims 12, 13, 28, 29, 44, 45.

III. Compounds where X is Nitrogen classified in 548/210 -Claims 14, 15, 30, 31, 46, 47.

IV. Compounds where X is methylene classified in 568/843 -Claims 16, 17, 32, 33, 48, 49. Claims 1, 18, 34, 50 and 60 are generic.

Each definition of X recites unique and distinct moieties for R which are distinct. A reference indicating an R moiety for group I. would not be applicable to one for group IV for example.